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ON THE CONDENSATION OF NITROMALONIC ALDEHYDE WITH BENZYLMETHYL KETONE.[1]

BY HENRY B. HILL AND WILLIAM J. HALE.

The condensation of various ketones with nitromalonic aldehyde has been the subject of much investigation in this laboratory. From the simpler reaction with acetone,[2] resulting in the ready formation of paranitrophenol, to the more involved cases with ketone acids,[3] the same mode of formation has been clearly made out, and no more confirmatory evidence regarding the nature of these condensations need be supplied. The formation of an intermediate product, a derivative of dihydrobenzol, seems established, which, by the addition and elimination of a molecule of water, passes into the phenol proper. The action of benzylmethyl ketone, in accordance with results just cited, must give a derivative of phenylbenzol, a 5-nitro-2-

[1] This paper was written after the untimely death of Professor Hill.—W. J. H.

[2] This JOURNAL, **22**, 89 (1899).

[3] *Ibid.*, **24**, 1 (1900).

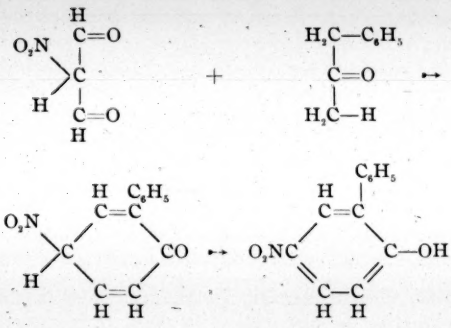
oxydiphenyl, and constitutes, therefore, an interesting field for the investigation of a number of hitherto unknown diphenyl derivatives.

Although this work was begun several years ago and a preliminary notice had appeared in the Spring of 1900,[1] an earlier article by Borsche[2] on the action of diazobenzol chloride upon an alkaline solution of nitrosophenol was found to overlap a portion of our work. As Borsche had not chosen to continue the study of the nitrodiphenyls it seemed advisable for us to turn our attention to the investigation of these compounds and to determine the relative positions of the nitro groups by comparison with the parent substance—the direct product of this synthesis.

The compound obtained by Borsche was a nitrosooxydiphenyl. From it he prepared the amido body, the quinone and hydroquinone, and by the action of nitric acid a dinitro derivative. These bodies have been obtained in the course of our investigations, but the melting-points are, in most instances, several degrees higher than those given by Borsche. In a second paper by Borsche[3] the conversion of the nitrosooxydiphenyl into the nitrooxydiphenyl by the action of very dilute nitric acid is described. This compound is the starting-point in our work, and results directly from the condensation of nitromalonic aldehyde with benzylmethylketone. The constitution of these compounds, as first determined by Borsche, appeared somewhat doubtful, but in the light of further investigations published in his second paper, and more particularly by these syntheses from nitromalonic aldehyde, the entire matter of constitution is definitely established.

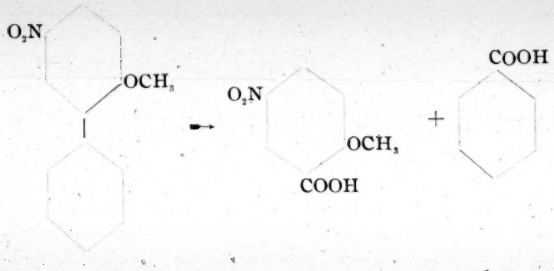
When benzylmethyl ketone reacts with sodium nitromalonic aldehyde, in slightly alkaline solution, there is formed the sodium salt of 1-phenyl-4-nitrophenol, *i. e.*, 5-nitro-2-oxydiphenyl. The first stage in this condensation must be considered as the formation of 1-nitro-3-phenyl-4-keto-Δ2,5-dihydrobenzol, which passes over at once into the phenol :

[1] Ber. d. chem. Ges., **33**, 1241 (1900).
[2] *Ibid.*, **32**, 2935 (1899).
[3] Ann. Chem. (Liebig), **312**, 211 (1900).

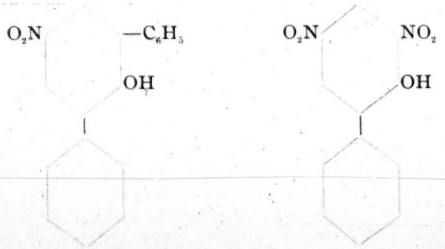


The phenol is readily liberated from the deep red solution of its sodium salt by means of a current of carbon dioxide. The sodium salt crystallizes in beautiful orange-red prisms, which change to crimson upon dehydration. The action of alkyl haloids upon this sodium salt, as well as that of benzoyl chloride upon the oxydiphenyl itself, gives mono derivatives which show conclusively but one hydroxyl present. From the nitro-oxydiphenyl was prepared the amido compound, and then the quinone, but owing to the appearance of Borsche's paper, further research in this line was discontinued and our attention given entirely to a study of the nitrooxydiphenyl itself.

When nitric acid acts upon 5-nitro-2-oxydiphenyl, in glacial acetic acid solution, another nitro group enters the substituted ring, and there is formed the 5,3-dinitro-2-oxydiphenyl. The nitro group naturally enters meta to the nitro group and ortho to the hydroxyl already present. The sodium salt of this dinitro compound crystallizes better than the sodium salt of the mononitro derivative, and appears in beautiful orange-red leaflets, containing 2 molecules of water of crystallization. The structure of the mononitrooxydiphenyl is readily established by the oxidation of its methyl ether with chromic acid mixture. The resulting products are 5-nitrosalicylic acid methyl ether, and benzoic acid,



In attempting to establish the constitution of the dinitro-oxydiphenyl by the oxidation of its ethers little or no oxidation-product could be obtained. In order, however, to substantiate the theory of its constitution an indirect method was adopted. The 2,6-diphenyl-4-nitrophenol of Soch and Oenslager[1] may be regarded as the 5-nitro-2-oxydiphenyl in which the 3-position is occupied by a phenyl group :

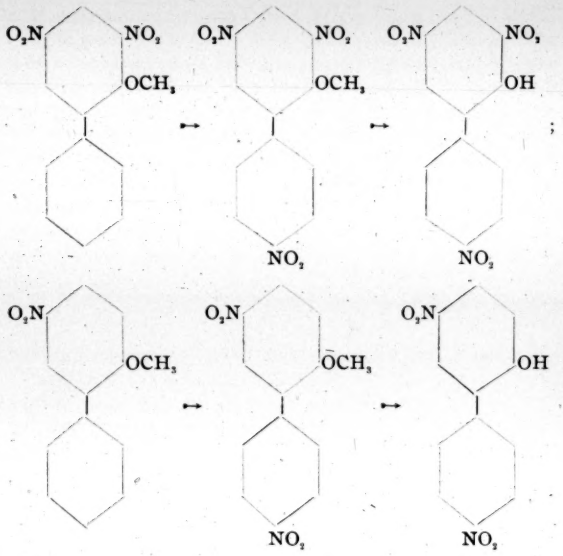


This body, on treatment with nitric acid in glacial acetic acid, does not give a dinitro compound such, for example, as was so easily obtained from 5-nitro-2-oxydiphenyl. As the 3-position—the only free position meta to the 5-nitro group—is the natural place for a second nitro group to enter, and as this position is already filled in the 5-nitro-2-oxy-1,3-diphenyl-

[1] This JOURNAL, **24**, 5 (1900).

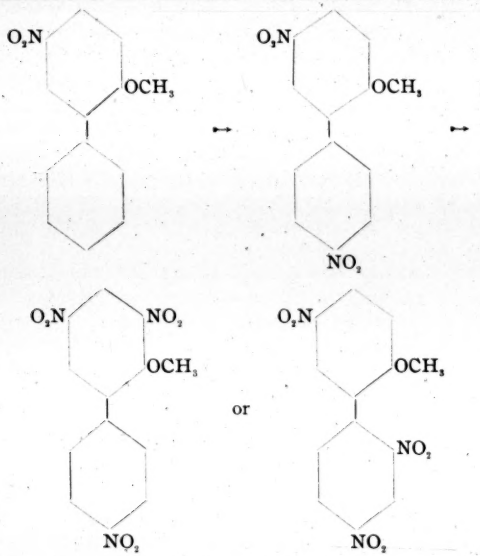
benzol of Soch and Oenslager, we have reason to believe that at this 3-position the second nitro group enters the 5-nitro-2-oxydiphenyl, forming thus a 5,3-dinitro-2-oxydiphenyl. When the mono- or dinitrooxydiphenyls are subjected to treatment with boiling nitric acid, the phenyl group bearing the hydroxyl is completely oxidized. Benzoic acid, however, or what might be expected in the presence of strong nitric acid—metanitrobenzoic acid—does not result, but in its place paranitrobenzoic acid is obtained. This is proof conclusive that the nitro group must have entered the free phenyl ring para to the tie existing before the oxidation took place. In order to establish the identity of this paranitrobenzoic acid the silver salt and methyl ester were made and analyzed.

The action of nitric acid upon the ethers was found to give additional nitro compounds and these, in turn, by saponification, could be converted into their corresponding nitrooxydiphenyls. The methyl ether of 5,3-dinitro-2-oxydiphenyl, on treatment with boiling nitric acid, passes into a 5,3,4′-trinitro-2-oxydiphenyl methyl ether. The free trinitrooxydiphenyl, obtained by the saponification of this ether, gave, on treatment with boiling nitric acid, paranitrobenzoic acid, which shows that the third nitro group must have entered the second ring para to the tie. When the 5-nitro-2-oxydiphenyl methyl ether is dissolved in glacial acetic acid and then treated with nitric acid, only one additional nitro group enters. This nitro group enters the second ring para to the tie, thus producing 5,4′-dinitro-2-oxydiphenyl methyl ether, which, in turn, may be converted into the free 5,4′-dinitro-2-oxydiphenyl by saponification with hydrochloric acid. 5,4′-Dinitro-2-oxydiphenyl is isomeric with 5-3-dinitro-2-oxydiphenyl and, by treatment with nitric acid in acetic acid solution, can be converted into 5,3,4′-trinitro-2-oxydiphenyl, the same compound as is obtained from the ether of 5,3-dinitro-2-oxydiphenyl. This is proof sufficient to show that in 5,4′-dinitro-2-oxydiphenyl the nitro group has entered the second ring para to the tie :



If the 5-nitro-2-oxydiphenyl methyl ether is treated with boiling nitric acid, the 5,4′-dinitro-2-oxydiphenyl methyl ether at first formed is converted, by further nitration, into a trinitro-2-oxydiphenyl methyl ether. This third nitro group can enter the first phenyl ring meta to the nitro group already present, and give 5,3,4′-trinitro-2-oxydiphenyl methyl ether; or it can enter the second phenyl ring meta to the nitro group that has previously entered, and thus produce a 5,2′4′-trinitro-2-oxydiphenyl methyl ether. As a matter of fact, both of these isomers are obtained in about equal quantity and can be readily separated by means of their respective solubilities in alcohol. The one, 5,3,4′-trinitro-2-oxydiphenyl methyl ether has already been mentioned; the other, 5,2′,4′-trinitro-2-oxydiphenyl methyl ether, was saponified with hydrochloric acid

and the free trinitro-2-oxydiphenyl subjected to oxidation by the action of boiling nitric acid. The benzoic acid formed proved to be metadinitrobenzoic acid, thus showing the relation of the two nitro groups in the second phenyl ring :



EXPERIMENTAL PART.

Benzylmethyl Ketone.[1]—Twenty to thirty grams phenyl acetic acid are boiled with a large excess of calcium carbonate in a liter of water. The hot, filtered solution is then evaporated to dryness upon a steam-bath, and the residue of calcium phenyl acetate dried at 120° to 130° for several hours. At this temperature the salt melts, and when cooled presents a vitreous appearance. The finely pulverized calcium phenyl acetate, deprived of its moisture, is now mixed with a large

[1] Ber. d. chem. Ges., 3, 198 (1870).

excess of pulverized calcium acetate, also dried at 120°. This mixture, placed in a non-tubulated retort, yields, on distillation, dibenzyl ketone, benzyl methyl ketone, and acetone. The dark-red, oily distillate thus obtained is freed of its acetone by warming upon a water-bath, and then shaken up, at ordinary temperatures, with four to five times its volume of a saturated aqueous solution of sodium acid sulphite. As ketones possessing methyl groups unite much more readily with acid sodium sulphite than do those without these groups, the crystalline product that separates on standing will consist entirely of the benzylmethyl ketone acid sulphite salt. Upon filtering off these crystals the dibenzyl ketone still adhering may be completely removed by washing with ether. The acid sodium sulphite salt of benzylmethyl ketone, by treatment with a strong solution of sodium carbonate, is readily resolved into neutral sodium sulphite and the free ketone, the latter rising to the surface as a colorless oily liquid which, after removal, should again be warmed on the water-bath to drive off any traces of acetone. Thirty grams calcium phenyl acetate, with 45 grams calcium acetate, gave 7.2 grams purified benzylmethyl ketone.

5-Nitro-2-oxydiphenyl, $C_6H_5.C_6H_3(NO_2)(OH)$.—A solution of sodium nitromalonic aldehyde[1] in six times its weight of water, to which has been added 1 molecule of sodium hydroxide in normal solution, is allowed to react with the equivalent amount of benzylmethyl ketone, dissolved in four to five times its weight of alcohol. The alcohol prevents the precipitation of the ketone by aqueous sodium hydroxide and thus enables the reaction to run to completion. The time necessary for this condensation is about twelve hours. A further addition of sodium hydroxide does not materially increase the yield of product nor shorten the time, while, with the alkali in amount less than 1 molecule, the time for complete reaction is considerably lengthened. The mixture does not require shaking, but reacts well by standing at ordinary temperatures. When reaction is complete the excess of alcohol is evaporated over the water-bath and the deep red liquid, cooled and some-

[1] This JOURNAL, **22**, 89 (1899).

what diluted by the addition of water, is saturated with carbon dioxide. The 5-nitro-2-oxydiphenyl soon separates as a yellow crystalline precipitate which, after removal to a filter, is well washed with cold water. In this manner 88.2 per cent of the theoretical yield was obtained. The use of hydrochloric acid for acidification proved undesirable, owing to the viscous form in which the phenol was precipitated.

5-Nitro-2-oxydiphenyl crystallizes best from dilute acetic acid in long, yellow needles, which melt at 125° to 126° (corr.), (126° to 128° Borsche).

It is readily soluble in acetone or in alcohol, and may be crystallized from dilute alcohol. It is fairly soluble in ether, chloroform, benzol, or carbon disulphide, but insoluble in ligroin. Boiling water dissolves it sparingly, 10,000 parts water dissolving 17.2 parts phenol, and from this aqueous solution the phenol again separates on cooling. 5-Nitro-2-oxydiphenyl sublimes beautifully in yellow needles.

I. 0.1791 gram substance gave 0.4408 gram CO_2 and 0.0732 gram H_2O.

II. 0.1462 gram substance gave 8.3 cc. moist N at 20° and 778 mm. pressure.

	Calculated for $C_{12}H_9O_3N$.	Found. I.	II.
C	66.94	67.14	....
H	4.22	4.57	....
N	6.55	....	6.62

The Sodium Salt of 5-Nitro-2-Oxydiphenyl.—The sodium salt is readily soluble in alcohol or water, and may be crystallized from its concentrated aqueous solution in the form of orange-red prisms which contain 3.5 molecules of water of crystallization. Nearly all of this crystal water is slowly lost over sulphuric acid, but to remove the last traces the salt must be dried at 120° to 125°. At the same time the orange-red color is changed into the crimson of the anhydrous salt.

I. 0.6676 gram salt lost, at 125°, 0.1398 gram H_2O.

II. 0.4858 gram salt lost, at 125°, 0.1020 gram H_2O.

III. 0.2324 gram air-dried salt gave 0.0551 gram Na_2SO_4.

	Calculated for $C_{12}H_8O_3NNa.3\frac{1}{2}H_2O$.	Found. I.	II.	III.
H_2O	21.01	20.94	21.00	....
Na	7.68	....	....	7.69

5-Nitro-2-oxydiphenyl Methyl Ether, $C_6H_5.C_6H_3(NO_2)(OCH_3)$.—The methyl ether is easily prepared by the action of methyl iodide upon the sodium salt. After three to four hours boiling upon the water-bath, under a reflux condenser, the clear solution is evaporated to dryness and extracted with ether. From the ethereal solution large clusters of needles separate on evaporation. The methyl ether is most readily soluble in hot alcohol, from which, on cooling, it crystallizes in beautiful colorless needles. It is insoluble in water, but readily soluble in ether, chloroform, acetone, benzol, or carbon disulphide, and fairly soluble in hot ligroin, from which also it may be crystallized. The melting-point is 95°.2 (corr.).

0.1585 gram substance gave 0.3972 gram CO_2 and 0.0726 gram H_2O.

	Calculated for $C_{13}H_{11}O_3N$.	Found.
C	68.09	68.36
H	4.84	5.12

5-Nitro-2-oxydiphenyl Ethyl Ether, $C_6H_5.C_6H_3(NO_2)(OC_2H_5)$.—This was prepared in the same manner as the methyl ether by the action of ethyl iodide upon the sodium salt. It is similar in its solubilities and in other respects to the methyl ether. After several crystallizations from alcohol the melting-point became constant at 110°.6 (corr.).

0.1414 gram substance gave 0.3576 gram CO_2 and 0.0702 gram H_2O.

	Calculated for $C_{14}H_{13}O_3N$.	Found.
C	69.10	68.98
H	5.39	5.55

5-Nitro-2-oxydiphenyl Benzoic Ether, $C_6H_5.C_6H_3(NO_2)(OCOC_6H_5)$.—When the 5-nitro-2-oxydi-

phenyl, made into a paste with a small amount of water, is shaken up with benzoyl chloride, and sufficient sodium hydroxide solution added to give an alkaline reaction, a precipitate is formed which, on crystallization from hot alcohol, appears in small, white, irregular prisms, melting at 99°.3 (corr.). This product is readily soluble in chloroform, carbon disulphide or hot alcohol, but insoluble in water. It is fairly soluble in benzol, ether, acetone, glacial acetic acid, or hot ligroin.

0.1772 gram substance gave 0.4628 gram CO_2 and 0.0692 gram H_2O.

	Calculated for $C_{19}H_{13}O_4N$.	Found.
C	71.45	71.24
H	4.11	4.37

5-Amido-2-oxydiphenyl, $C_6H_5.C_6H_3(NH_2)(OH)$.—The 5-nitro-2-oxydiphenyl was reduced to the amido compound by tin and hydrochloric acid in alcoholic solution; gentle warming greatly facilitates the reduction. After the tin has been removed by the action of hydrogen sulphide, and the mother-liquor sufficiently concentrated, crystals of the hydrochlorate appear. This gives, by treatment with a solution of potassium carbonate, a white precipitate of the free base which, owing to impurities present, rapidly darkens on exposure to the air. 5-Amido-2-oxydiphenyl is fairly soluble in carbon disulphide or in hot benzol, crystallizing from the latter as the solution cools. It is sparingly soluble in ether or chloroform, insoluble in ligroin or water, but soluble in hot alcohol, from which it crystallizes well in small, colorless needles, melting at 198° to 199° (corr.) (192° Borsche).

0.1388 gram substance gave 0.3945 gram CO_2 and 0.0798 gram H_2O.

	Calculated for $C_{12}H_{11}ON$.	Found.
C	77.79	77.52
H	5.98	6.43

2-Phenylbenzoquinone, $C_6H_5.C_6H_3O_2$.—The 5-amido-2-oxydiphenyl, dissolved in forty times its weight of dilute sulphuric

acid (1 part acid to 3 parts water), was treated with sodium dichromate, in excess of the requisite amount, dissolved in four times its weight of water. Gentle warming upon the water-bath was found necessary to start the reaction. The mixture was then allowed to stand several hours, after which the quinone was removed by extraction with ether. 2-Phenylbenzoquinone is readily soluble in ether, chloroform, or carbon disulphide, and fairly soluble in ligroin, benzol, acetone, or hot water, crystallizing from water on cooling. It dissolves readily in warm alcohol, and crystallizes from it slowly, but is best crystallized out of dilute acetic acid (80 per cent), from which it separates in orange-yellow leaflets, melting at 112° to 113° (corr.) (107° to 108° Borsche).

0.1112 gram substance gave 0.3184 gram CO_2 and 0.0488 gram H_2O.

	Calculated for $C_{12}H_8O_2$.	Found.
C	78.24	78.11
H	4.38	4.91

5,3-Dinitro-2-oxydiphenyl, $C_6H_5.C_6H_2.(NO_2)_2.(OH)$. — The 5-nitro-2-oxydiphenyl was dissolved in twelve to fifteen times its weight of glacial acetic acid by gently warming, and four to five times its weight of nitric acid (sp. gr. 1.40) then added. From this warm solution there separates, almost immediately, yellow crystals of the dinitrooxydiphenyl. The product is obtained in a very pure condition, and in an amount equal to 95 per cent of the theoretical. This dinitrooxydiphenyl sublimes in the form of yellow needles like the mononitrooxydiphenyl, but with less ease. It is sparingly soluble in ether or carbon disulphide, insoluble in ligroin, and very sparingly soluble in hot water. It dissolves in benzol, chloroform, acetone, alcohol, ethyl acetate, or glacial acetic acid when hot, and from each crystallizes on cooling. The crystals obtained from acetone or ethyl acetate are in the form of small elongated octahedra, while from alcohol, benzol, or glacial acetic acid they appear in long, saw-teeth aggregations. From glacial acetic acid, its best solvent, the purified product melts at 207° to °208 (corr.)(203° to 204° Borsche).

I. 0.2144 gram substance gave 0.4338 gram CO_2 and 0.0654 gram H_2O.

II. 0.2286 gram substance gave 22.1 cc. moist N at 23° and 775 mm. pressure.

	Calculated for $C_{12}H_8O_5N_2$.	Found. I.	II.
C	55.36	55.17	....
H	3.10	3.41	....
N	10.80	....	11.06

The Sodium Salt of 5,3-Dinitro-2-oxydiphenyl.—By dissolving the dinitrooxydiphenyl in a hot solution of sodium hydroxide it is at once converted into the sodium salt which separates as the solution cools. The sodium salt, though fairly soluble in hot water, is only sparingly soluble in cold. It crystallizes beautifully from its aqueous solution in glistening, orange-red leaflets, which lose their water of crystallization slowly over sulphuric acid, more rapidly at 100° to 105°, and change color to the crimson of the anhydrous salt. A solution of the sodium salt may be decomposed by carbon dioxide and the dinitrooxydiphenyl thus liberated.

I. 0.4924 gram air-dried salt lost, at 100° to 105°, 0.0554 gram H_2O.

II. 0.2408 gram air-dried salt lost, at 100° to 105° in two hours, 0.0272 gram H_2O.

III. 0.2438 gram air-dried salt gave 0.0542 gram Na_2SO_4.

	Calculated for $C_{12}H_7O_5N_2Na.2H_2O$.	Found. I.	II.	III.
H_2O	11.32	11.25	11.30	....
Na	7.24	....	....	7.21

5,3-Dinitro-2-oxydiphenyl Methyl Ether, $C_6H_5.C_6H_2.(NO_2)_2.(OCH_3)$.—By the action of methyl iodide upon the sodium salt of dinitrooxydiphenyl, the methyl ether is formed, but the reaction runs too slowly for practical purposes. The silver salt, prepared by the action of silver nitrate upon a solution of the sodium salt, was found to work much better, and accordingly was treated with methyl iodide and methyl alcohol, under a reflux-condenser, upon a water-bath. After boiling for several hours, the clear alcoholic solution was

poured off and evaporated; small yellow crystals of the methyl ether soon separate, which, after repeated crystallization from alcohol, are obtained in colorless leaflets, melting at 114° to 115° (corr.). This methyl ether is fairly soluble in ether or in hot ligroin, and from the latter it may be crystallized. It is insoluble in water, but quite readily soluble in benzol or glacial acetic acid, crystallizing fairly well from 40 per cent acetic acid.

0.2356 gram substance gave 0.4902 gram CO_2 and 0.0832 gram H_2O.

	Calculated for $C_{13}H_{10}O_5N_2$.	Found.
C	56.90	56.75
H	3.67	3.95

5,3-Diamido-2-oxydiphenyl, $C_6H_3.C_6H_2.(NH_2)_2.(OH)$.—The reduction of the dinitrooxydiphenyl by tin and hydrochloric acid was carried on in alcoholic solution in the same manner as described in the reduction of the mononitrooxydiphenyl. The colorless crystals of the hydrochlorate thus obtained, upon treatment with potassium carbonate, gave a yellow flocculent precipitate, which changed rapidly to a reddish-brown powder when dry. The diamidooxydiphenyl is soluble in alcohol or in glacial acetic acid, insoluble in ether, ligroin, or chloroform. The alcoholic solution, on dilution with water, gave a brown-red precipitate, but no definitely crystalline substance with a melting-point could be obtained.

Oxidation of the 5-Nitro-2-oxydiphenyl Methyl Ether.—In attempting to oxidize the free phenyl group in this compound, by the use of potassium permanganate in neutral or in alkaline solution, no successful results were obtained. In all cases the methyl ether remained unacted upon and could be completely recovered. The use of chromic acid in acetic acid solution, as carried out by Hammarsten,[1] proved much more satisfactory than the usual method of potassium dichromate with sulphuric acid. Under such conditions the methyl ether was readily resolved into the acids possible from the two phenyl rings. Mononitrooxydiphenyl methyl ether was boiled vigor-

[1] Ber. d. chem. Ges., 14, 71 (1881).

ously, under a reflux condenser, with forty times its weight of 20 per cent solution of chromium trioxide dissolved in glacial acetic acid. After a half hour's boiling the cooled solution was poured into a small quantity of water and the aqueous mixture extracted with ether. The residue from the ether extract was then treated with a solution of sodium carbonate to dissolve the acid oxidation-products, and, at the same time, to leave undissolved the unchanged methyl ether. In this case the absence of methyl ether indicated that the oxidation was complete. The clear solution of the sodium salts, after acidification with hydrochloric acid, was again extracted with ether, and afforded a white product melting at 125° to 140°. This product was now distilled with steam; all of it dissolved readily in the hot water and a portion which distilled over with the aqueous vapor after extraction from the distillate by ether, proved to be benzoic acid, melting sharply at 120°. The contents of the flask, on extraction with ether, gave a white solid melting at 147° to 149°, evidently the 5-nitrosalicylic acid methyl ether melting at 148° to 149°.[1]

Oxidation of the 5,3-Dinitro-2-oxydiphenyl Methyl Ether.—This proved to be a much more difficult task. Even with the strongest chromic acid mixtures no appreciable quantity of acid oxidation products was taken up by the sodium carbonate solution as previously employed. In all cases the residue was the unchanged methyl ether. Although 5,3-dinitrosalicylic acid methyl ether may have been produced in this manner, the quantity was insufficient for its complete identification.

Nitric Acid and the Nitrooxydiphenyls.—The dinitrooxydiphenyl undergoes vigorous oxidation when boiled for fifteen to twenty minutes, with twenty times its weight of nitric acid (sp. gr. 1.40), in a long-necked flask, the neck serving as a reflux condenser. A large amount of carbon dioxide is evolved, and on cooling small white crystals of paranitrobenzoic acid separate from the reaction-mixture. In like manner the mononitrooxydiphenyl, heated with twenty times its weight of strong nitric acid, gives the same result, but as this compound does not dissolve readily in the nitric acid, the time

[1] Ann. Chem. (Liebig), **180**, 6 (1869); **173**, 41 (1874).

necessary for the oxidation is about twice that required for the dinitrooxydiphenyl. The crystalline product in each case melted at 226° to 234°. It crystallizes from water in leaflets and melts at 233° to 234°, whereas paranitrobenzoic acid melts at 238°.

0.2178 gram substance gave 0.3982 gram CO_2 and 0.0612 gram H_2O.

	Calculated for $C_7H_5O_4N$.	Found.
C	50.27	49.84
H	3.02	3.14

The silver salt of this oxidation product was made by first forming the ammonium salt and then precipitating the aqueous solution with silver nitrate. It was purified by crystallization from hot water, from which it separated in white needle clusters.

0.1775 gram silver salt, dried over sulphuric acid, gave 0.1222 gram AgBr.

	Calculated for $C_7H_4O_4NAg$.	Found.
Ag	39.38	39.55

As a further means of identification the methyl ester of this oxidation product was made. Not only from the silver salt by treatment with methyl iodide, but also from the free acid itself by the action of hydrochlorated methyl alcohol; the product obtained was the methyl ester of paranitrobenzoic acid. This ester is readily soluble in ether, benzol, alcohol, or hot ligroin, and after crystallization from ligroin or dilute alcohol appears in glistening leaflets, which melt at 94° to 95°. The melting-point given by Beilstein is 96°. The identity of the products obtained by these two methods shows conclusively that there is no phenolic hydroxyl present, and therefore leads to the conclusion that the phenyl ring bearing the hydroxyl in the original nitrooxydiphenyl is completely broken up. The production of paranitrobenzoic acid would naturally point to the presence of some ortho- or metanitrobenzoic acid in the oxidation mixture, but no meta-acid whatever was found, and

only the smallest traces of orthonitrobenzoic acid could be isolated from the mother-liquors.

Action of Nitric Acid upon the Nitrooxydiphenyl Methyl Ethers.

5,3,4'-Trinitro-2-oxydiphenyl Methyl Ether, $C_6H_4(NO_2).C_6H_2(NO_2)_2.(OCH_3)$. — The 5,3-dinitro-2-oxydiphenyl methyl ether was boiled under a reflux condenser for twenty minutes with twenty times its weight of nitric acid (sp. gr. 1.40). From the reaction mixture, transferred to an open vessel and concentrated over the water-bath to one-third its volume, small, elongated prisms separate on cooling, which melt at 165° to 167°, but on further crystallization from glacial acetic acid melt at 170° to 171° (corr.). The yield is almost quantitative. This trinitrooxydiphenyl methyl ether is readily soluble in chloroform, ethyl acetate, or boiling glacial acetic acid, fairly soluble in benzol, and only sparingly soluble in ether or boiling alcohol. It is insoluble in ligroin or water.

0.1352 gram substance gave 0.2420 gram CO_2 and 0.0386 gram H_2O.

	Calculated for $C_{13}H_9O_7N_3$.	Found.
C	48.88	48.82
H	2.84	3.19

5,3,4'-Trinitro-2-oxydiphenyl, $C_6H_4(NO_2).C_6H_2(NO_2)_2.(OH)$. —When the trinitrooxydiphenyl methyl ether, melting at 170° to 171°, is heated with a large excess of concentrated hydrochloric acid, in a sealed tube, at 180° to 190°, for from six to seven hours, saponification takes place and there is formed the free trinitrooxydiphenyl and methyl chloride. The contents of the tube, were diluted with water, filtered, and the yellow product collected. This trinitrooxydiphenyl was dissolved by warming in a solution of sodium hydroxide ; the clear red liquid thus obtained showed that the saponification was complete ; after acidification with hydrochloric acid, the yellow precipitate of trinitrooxydiphenyl was crystallized from hot alcohol ; it melts at 163° to 164° (corr.), and consists of pointed, light yellow prisms, irregular in form. It is readily soluble in benzol, ether, or chloroform, fairly soluble in glacial acetic acid or

carbon disulphide, and insoluble in ligroin or water. It may also be crystallized from dilute acetic acid. The sodium salt of this compound is soluble in alcohol, and though readily soluble in hot water, is only fairly so in cold, crystallizing from water in matted globular aggregations of an orange-red color.

0.1818 gram substance gave 0.3138 gram CO_2 and 0.0454 gram H_2O.

	Calculated for $C_{12}H_7O_7N_3$.	Found.
C	47.18	47.08
H	2.31	2.79

5,3,4'-Trinitro-2-oxydiphenyl, on treatment with twenty times its weight of boiling nitric acid (sp. gr. 1.40), for some twenty minutes, gave crystals of paranitrobenzoic acid, melting at 235° to 238°.

5,4'-Dinitro-2-oxydiphenyl Methyl Ether, $C_6H_4(NO_2).C_6H_3(NO_2).(OCH_3)$.—A solution of 5-nitro-2-oxydiphenyl methyl ether, in ten times its weight of glacial acetic acid, was treated with three to four times its weight of nitric acid (sp. gr. 1.40), and after gentle boiling for some ten to twelve minutes under a reflux condenser, was allowed to cool. A white crystalline mass of needle-clusters readily separated. The same product may be obtained when the 5-nitro-2-oxydiphenyl methyl ether is dissolved in concentrated nitric acid, but the solution must be immediately diluted with water and rapidly cooled, in order to prevent further nitration. 5,4'-Dinitro-2-oxydiphenyl methyl ether is soluble in one hundred parts of hot alcohol, from which it crystallizes in very fine white needles. It is soluble in warm glacial acetic acid, or in hot benzol, crystallizing from each as the solution cools. It is also readily soluble in chloroform, sparingly in ether, and insoluble in ligroin or water. After repeated crystallization from alcohol the melting-point became constant at 222° to 223° (corr.).

0.1560 gram substance gave 0.3247 gram CO_2 and 0.0546 gram H_2O.

	Calculated for $C_{13}H_{10}O_5N_2$.	Found.
C	56.90	56.80
H	3.67	3.91

5,4'-Dinitro-2-oxydiphenyl, $C_6H_4(NO_2).C_6H_3(NO_2).(OH)$.—The 5,4'-dinitro-2-oxydiphenyl methyl ether is converted into the free oxydiphenyl by heating for from five to six hours with concentrated hydrochloric acid, in a sealed tube, at 200 to 210°. The product, filtered from the diluted acid mixture, was dissolved by warming with a solution of sodium hydroxide. This clear red liquid, filtered from traces of unsaponified methyl ether, was then acidified with hydrochloric acid to reprecipitate the nitrooxydiphenyl. 5,4'-Dinitro-2-oxydiphenyl crystallizes best from dilute alcohol (50 per cent.) in long slender needles, of a pale yellow color, melting at 224° to 225° (corr.). It is readily soluble in alcohol, ether, chloroform, or glacial acetic acid, moderately soluble in hot benzol, and insoluble in ligroin or water.

0.1284 gram substance gave 0.2596 gram CO_2 and 0.0380 gram H_2O.

	Calculated for $C_{12}H_8O_5N_2$.	Found.
C	55.35	55.14
H	3.10	3.31

The sodium salt is fairly soluble in cold water, and readily so in hot, crystallizing out in small orange-red needle clusters. When 5,4'-dinitro-2-oxydiphenyl is boiled with twenty times its weight of nitric acid (sp. gr. 1.40) paranitrobenzoic acid results, as in the oxidation of the nitrooxydiphenyls previously described. If, however, the compound is dissolved in glacial acetic acid, and a small quantity of nitric acid added, there separates, upon dilution with water, a yellow precipitate of the 5,3,4'-trinitro-2-oxydiphenyl melting at 163° to 164°, the same product as is obtained from the 5,3-dinitro-2-oxydiphenyl.

5,2',4'-Trinitro-2-oxydiphenyl Methyl Ether, $C_6H_3(NO_2)_2.C_6H_3(NO_2)(OCH_3)$.—When 5-nitro-2-oxydiphenyl methyl ether is boiled under a reflux condenser, for twenty-five to thirty minutes, with twenty times its weight of nitric acid (sp. gr. 1.40), and the solution, after evaporation to one-third its volume over the water-bath, is allowed to stand, there separates a white crystalline product, melting at 105° to 120°. These crystals, dried and finely powdered, were extracted with

a considerable quantity of warm alcohol. The residue, after several crystallizations from glacial acetic acid, melted at 170° to 171° (corr.), and is therefore the 5,3,4′-trinitro-2-oxydiphenyl methyl ether. The clear alcoholic solution, on evaporation, gave a white crystalline product, which, after several crystallizations from alcohol, appeared in small flattened prisms, melting at 104° to 106° (corr.). The two compounds thus isolated are produced in equal quantities, and in almost quantitative yields. The same results are obtained when the 5,4′-dinitro-2-oxydiphenyl methyl ether is treated with boiling nitric acid; therefore the compounds are seen to be isomeric. 5,2′,4′-Trinitro-2-oxydiphenyl methyl ether is readily soluble in chloroform, ether, benzol, ethyl acetate, glacial acetic acid, or hot alcohol, but almost insoluble in ligroin. It may be crystallized from benzol and ligroin, and also from dilute acetic acid.

0.1392 gram substance gave 0.2483 gram CO_2 and 0.0392 gram H_2O.

	Calculated for $C_{13}H_9O_7N_3$.	Found.
C	48.88	48.66
H	2.84	3.15

5,2′,4′-Trinitro-2-oxydiphenyl, $C_6H_3(NO_2)_2.C_6H_3(NO_2)(OH)$. —This compound results upon the saponification of 5,2′,4′-trinitro-2-oxydiphenyl methyl ether with concentrated hydrochloric acid. The reaction is conducted in a sealed tube, at a temperature of 160° to 170°, for five or six hours. The crude product was dissolved in a solution of sodium hydroxide, and the clear red solution of the sodium salt acidified with hydrochloric acid, the nitrooxydiphenyl separating as a pale yellow precipitate. It is readily soluble in chloroform, fairly so in glacial acetic acid, warm alcohol, or warm benzol, sparingly in ether, and insoluble in ligroin. It crystallizes from dilute acetic acid, but better from benzol and ligroin, in small pointed yellow prisms, melting at 152° to 153° (corr.). The sodium salt is fairly soluble in cold water, readily so in hot, and crystallizes in small orange-red needle-clusters.

0.1030 gram substance gave 0.1780 gram CO_2 and 0.0254 gram H_2O.

	Calculated for $C_{19}H_7O_7N_3$.	Found.
C	47.18	47.14
H	2.31	2.66

When this 5,2′,4′-trinitro-2-oxydiphenyl is boiled with twenty times its weight of nitric acid (sp. gr. 1.40), for twenty to thirty minutes, and the reaction mixture cooled, white crystals of 2,4-dinitrobenzoic acid separate. After crystallization from dilute acetic acid the melting-point rose to that of the pure acid, 179°. This indicates that the two nitro groups in the second phenyl ring are meta to one another.

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND UNSATURATED COMPOUNDS.

II. REACTIONS WITH DERIVATIVES OF CINNAMIC ACID.

By E. P. Kohler and Gertrude Heritage.

The experiments described below were made in continuation of a study of the properties of substances containing the conjugated system,

$$C : C.C : O.$$

In the first paper[1] it was shown that the reaction between substances of this type and organic magnesium compounds varies in a remarkable way with the atoms or groups in combination with the carbon atom of the carbonyl group. The reaction is always one of direct addition, but in the case of aldehydes and of those ketones that contain the group

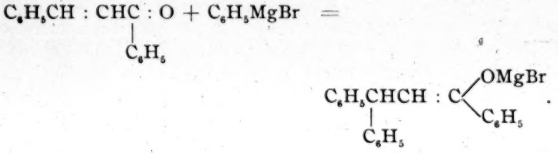
$$—CH : CH.\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} : O,$$

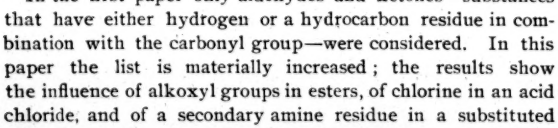
the magnesium compound combines exclusively with the car-

[1] This Journal, **31**, 642.

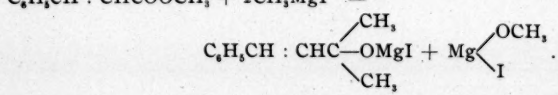
bonyl group, while only 1,4-addition takes place when the ketone contains the group

Two typical reactions are illustrated by the following equations:





In the first paper only aldehydes and ketones—substances that have either hydrogen or a hydrocarbon residue in combination with the carbonyl group—were considered. In this paper the list is materially increased; the results show the influence of alkoxyl groups in esters, of chlorine in an acid chloride, and of a secondary amine residue in a substituted acid amide. It will be seen that the principal reaction with all of these substances consists in 1,4-addition of the magnesium compound to the conjugated system. The reactions of methylmagnesium iodide apparently form an exception, as these invariably give magnesium derivatives of an unsaturated tertiary alcohol:



The reason for this is evident. The magnesium compound which, as is known, reacts considerably more readily than the corresponding aromatic compounds, first replaces the methoxyl group with methyl:

$$C_6H_5CH : CHC(OCH_3) : O + CH_3MgI = C_6H_5CH : CHC(CH_3) : O + CH_3OMgI.$$

The result is an unsaturated ketone of the type that gives only 1,2-addition-products with magnesium compounds. This explanation is supported by the fact that, when the ordinary method of procedure is reversed, so that the magnesium compound is gradually added to an excess of the ester, it is possible to isolate a considerable quantity of the unsaturated ketone.

The method of proving that 1,4-addition had taken place in any given case, was the same as that used in the work described in the previous paper; the magnesium compound was treated with benzoyl chloride, and the formation of an ester of benzoic acid was regarded as proof that the magnesium had been in combination with oxygen. In support of this method, it has been found that when magnesium compounds, in which the magnesium is undoubtedly linked to oxygen, are treated with benzoyl chloride under the same conditions, they readily react to form esters of benzoic acid. When benzaldehyde, for example, reacts with phenylmagnesium bromide, the product must have the magnesium linked to oxygen because it gives benzhydrol when decomposed with water. When the magnesium compound before decomposition with water, is treated with benzoyl chloride, it gives a very good yield of benzhydrol benzoate:

$$(C_6H_5)_2CHOMgBr + C_6H_5COCl = (C_6H_5)_2CHOCOC_6H_5 + MgBrCl.$$

The magnesium compounds described below are, so far as

we know, the only 1,4-addition-products of α,β-unsaturated acids that have thus far been obtained. Their formation and properties lend strong support to Thiele's view that the "apparent activity" of the double union between the carbon atoms of this type of unsaturated acids is due to the possibility of 1,4-addition to the conjugated system,

$$C{=}C{-}C{=}O.$$

In most cases the product formed by 1,4-addition to this group immediately undergoes rearrangement, but, by reason of its peculiar composition, a magnesium compound, like that represented by the formula

$$(C_6H_5)_2CH{-}CH : C\begin{matrix}OMgBr\\OCH_3\end{matrix},$$

is stable. The corresponding acyl derivatives are also capable of existence, hence there is no rearrangement when the magnesium compound reacts with an acid chloride :

$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!CH{-}CH{=}C\begin{matrix}OMgBr\\OCH_3\end{matrix} + ClCOC_6H_5 =$$

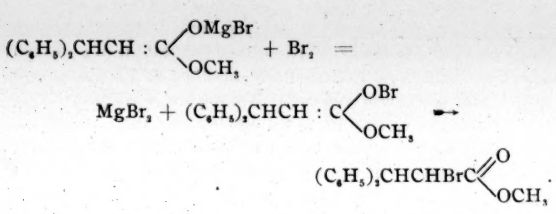
$$MgBrCl + \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!\!>\!CH{-}CH{=}C\begin{matrix}OCOC_6H_5\\OCH_3\end{matrix}.$$

The corresponding hydrogen and halogen compounds, on the other hand, represent types that are, as is known, extremely unstable, hence the products formed by the action of water, of acids and of the halogens, on these magnesium compounds, immediately undergo rearrangement into a more stable form :

$$(C_6H_5)_2CHCH : C\begin{matrix}OMgBr\\OCH_3\end{matrix} + HX =$$

$$Mg\begin{matrix}Br\\X\end{matrix} + (C_6H_5)_2CHCH : C\begin{matrix}OH\\OCH_3\end{matrix} \rightarrow$$

$$(C_6H_5)_2CHCH_2C\begin{matrix}O\\OCH_3\end{matrix};$$



Before describing the experiments we desire to point out that this paper deals only with the primary products obtained by the reaction under consideration. The addition-products, obtained by 1,4-addition of magnesium compounds to unsaturated compounds, as a rule, readily combine with more of the unsaturated compound and, unless special precautions are taken, the final result is a mixture of a number of exceedingly complex substances. With methyl cinnamate and phenylmagnesium bromide, for example, we have obtained no less than five of these complex secondary products that we expect to consider in a subsequent paper.

EXPERIMENTAL.

I. Reactions with Esters.

Methyl Cinnamate and Phenylmagnesium Bromide: Methyl β,β-Diphenylpropionate, $(C_6H_5)_2CHCH_2COOCH_3$.—A dilute ethereal solution of the ester was added, drop by drop, to a solution of the magnesium compound that was kept at —10° in a freezing-mixture. Each drop of the ester produced a yellow precipitate that redissolved until the liquid contained somewhat more than 1 molecule of ester for 2 molecules of the magnesium compound. At this stage the yellow compound no longer disappeared even after vigorous shaking, hence the addition of ester was discontinued. The liquid was allowed to remain in the freezing-mixture for two hours, and for one more hour at the ordinary temperature. It was then poured into a separating funnel containing finely crushed ice and shaken until the magnesium compound was completely decomposed. After dissolving the magnesium salts in iced hydrochloric acid, the

ethereal layer was separated washed, and dried with sodium sulphate. The ethereal solution, on evaporation in a current of dry air, left an oil that partially solidified in a freezing-mixture. The solid was removed as completely as possible by adding low-boiling ligroin to the oil and filtering. After one recrystallization from alcohol it was found to be pure diphenylpropiophenone. The ligroin was evaporated and the oily residue exposed to a low winter temperature for several days, when it solidified almost completely. The solid was dried on a porous plate, and recrystallized from a mixture of ligroin and ether. An analysis gave the following results:

0.1640 gram substance gave 0.4798 gram CO_2 and 0.1004 gram H_2O.

	Calculated for $C_{16}H_{16}O_2$.	Found.
C	80.00	79.73
H	6.66	6.79

The substance has the composition of a methyl ester of diphenylpropionic acid. It gave β,β-diphenylpropionic acid when hydrolyzed, and it was further identified by comparison with a specimen of the ester obtained by boiling β,β-diphenylpropionic acid with a 3 per cent. solution of hydrochloric acid in methyl alcohol. The ester crystallizes from ether or ligroin in large lustrous prisms that melt at 47°. It is readily soluble in alcohol, ether, and boiling ligroin; moderately soluble in cold ligroin.

These results show that the phenyl group in the magnesium compound goes to one end of the conjugated system, but they do not indicate the fate of the magnesium atom. To locate this the magnesium compound was prepared as before, and treated with an ethereal solution of benzoyl chloride, containing 1 molecule of the chloride for each atom of magnesium used in the preparation of phenylmagnesium bromide. The reaction took place in the cold, the product separating as a crystalline solid. This was filtered off, washed with dilute hydrochloric acid and recrystallized from acetone. It was thus separated into two benzoyl compounds, one of which—the less

soluble—was the benzoic acid ester described in a previous paper. The more soluble substance is much less stable. After repeated solution in cold acetone and precipitation with absolute alcohol it was obtained in long, silky, white needles, melting at 130° to 133°. An analysis gave the following results:

0.1591 gram substance gave 0.4668 gram CO_2 and 0.0861 gram H_2O.

	Calculated for $C_{23}H_{20}O_2$.	Found.
C	80.23	80.00
H	5.83	6.01

The compound is evidently a benzoate, since it is very easily hydrolyzed to benzoic acid and methyl diphenylpropionate. For this purpose it is sufficient to suspend the substance in water and distil in a current of steam; benzoic acid passes into the distillate while pure diphenylpropionic ester remains behind. These results may be summed up as follows:

1. Some of the ester reacts with phenylmagnesium bromide like an ester of a saturated acid, giving the corresponding ketone:

$$C_6H_5CH : CHCOOCH_3 + C_6H_5MgBr = C_6H_5CH : CHCOC_6H_5 + MgOCH_3Br.$$

This ketone immediately combines with a second molecule of the magnesium compound:

$$C_6H_5CH : CHCOC_6H_5 + C_6H_5MgBr = (C_6H_5)_2CH.CH : C(OMgBr)C_6H_5.$$

2. The rest of the ester combines directly with the magnesium compound:

$$C_6H_5CH : CH\underset{\displaystyle OCH_3}{\underset{|}{C}}O + C_6H_5MgBr = (C_6H_5)_2CHCH : C(OMgBr)OCH_3.$$

The relative amounts of ketone and ester formed vary with the temperature. At —10° the amount of ketone obtained rarely exceeds 5 per cent. of the entire product, while at the temperature of boiling ether, the amount may rise to 20 per cent.

The relative amounts of ketone and ester produced also vary with the different esters of cinnamic acid. The ethyl ester gives only a trace of ketone at —10°, and less than 10 per cent at the temperature of boiling ether. The amyl ester gives only a trace of ketone at the higher, and none at the lower temperature.

Methyl Cinnamate and Methylmagnesium Iodide: Dimethylstyril Carbinol: $C_6H_5CH:CHC(CH_3)_2OH$.—The substances were allowed to react under a variety of different conditions. In some experiments an ethereal solution of the ester was gradually added to an excess of the magnesium compound at the temperature of a freezing-mixture; in others the reaction was carried out in boiling ether and in still others in boiling benzene. The result was the same in all cases. After removing the magnesium salts and evaporating the ether, there remained an oil from which no solid substances could be obtained and which could not be distilled, even in a vacuum, without decomposition. As the oil was not hydrolyzed when boiled with alcoholic potash, it contained no ester, and because it gave no oxime when boiled with an alcoholic solution of hydroxylamine hydrochloride and potassium hydroxide, it contained no ketone. It readily reduced cold alkaline solution of potassium permanganate.

Twenty grams of the oil, suspended in ice-water, were treated with a cooled solution of potassium permanganate until no further reduction took place. Nearly all of the oil went into solution; the rest was extracted with ether. The oxides of manganese were filtered off and the filtrate concentrated on a water-bath. On acidifying the concentrated solution benzoic acid was precipitated. This was filtered off and a small quan-

tity of the same acid that remained in solution removed by distillation in a current of steam. From the liquid left after distillation ether extracted a different acid, which remained as a crystalline solid when the ether was evaporated. This was found to be oxyisobutyric acid. It melted at 79° and sublimed at the temperature of the water-bath. These oxidation-products—benzoic and oxyisobutyric acids—show that the reaction between methyl cinnamate and methylmagnesium iodide, results mainly in the formation of the tertiary alcohol, $C_6H_5CH : CHC(CH_3)_2OH$, the oxidation taking place at the double linkage.

The part of the product that was not affected by the oxidizing agent was less than 5 per cent of the whole. It was a volatile oil, with a very pronounced, characteristic odor and was not formed by the permanganate because the same oil was obtained by distilling the original product in a current of steam. It boils under diminished pressure without decomposition, most of it distilling at 128° under a pressure of 11 mm. The fraction boiling at this temperature gave the following results on analysis :

0.1611 gram substance gave 0.5086 gram CO_2 and 0.1264 gram H_2O.

	Calculated for $C_{22}H_{26}O$.	Found.
C	86.28	86.10
H	8.50	8.72

The composition of the substance corresponds to that of an ether represented by the formula $[C_6H_5CH : C(CH_3)_2]_2O$. The substance combines with bromine and reduces boiling alkaline solution of potassium permanganate. Since it is evidently a very subordinate product of the reaction, it was not investigated any further.

When an ethereal solution of methylmagnesium iodide is slowly siphoned into a solution of the ester that is kept in a freezing-mixture, the product contains a considerable quantity

of benzalacetone, in addition to the substances described above. This was isolated as follows: The oil was first distilled with steam to remove the ether, then dried in an evaporating dish on the water-bath and repeatedly extracted with low-boiling ligroin. The ligroin solution, on evaporation, left an oil that partially solidified when seeded with a crystal of benzalacetone. The solid was dried on a porous plate and recrystallized from ligroin. It melted sharply at 36°, the melting-point of benzalacetone, and gave dibenzalacetone with benzaldehyde and sodium hydroxide. The yield was small 4.8 grams of ketone from 20 grams of methyl cinnamate.

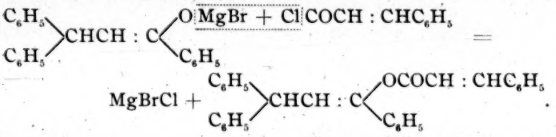
II. Reactions with Cinnamyl Chloride.

Cinnamyl Chloride and Phenylmagnesium Bromide.—The substances reacted energetically when brought together in dilute ethereal solution at —20°. The product, separated in the usual way, was a thick viscous liquid that evidently contained a number of different substances. After removing some brombenzene and diphenyl by distillation in a current of steam and a small quantity of cinnamic acid by extraction with boiling water, the remainder of the product was boiled for two hours with alcoholic potash, and the solution evaporated to dryness. A partial separation of the residue was obtained by boiling with water and filtering. The part that was insoluble in water—approximately 20 per cent of the entire product—was recrystallized from alcohol. It was mainly diphenylpropiophenone mixed with complex substances that were not investigated.

From the aqueous solution, which contained potassium chloride and potassium salts of organic acids, dilute hydrochloric acid precipitated two acids that were separated by fractional recrystallization from boiling water. One was cinnamic acid, the other β,β-diphenylpropionic acid.

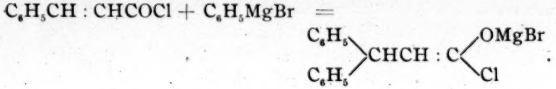
It is evident, from these results, that the primary reactions of cinnamylchloride are exactly like those of the esters of cinnamic acid. A part of the chloride reacts like chlorides of

saturated acids and forms an unsaturated ketone—benzalacetophenone. This combines with a second molecule of phenylmagnesium bromide to form a magnesium compound that, in turn, reacts with a second molecule of the chloride :



When the resulting cinnamate is boiled with alcoholic potash it gives potassium cinnamate, and diphenylpropiophenone.

Another part of the acid chloride combines directly with phenylmagnesium bromide.



The resulting magnesium compound also reacts with an additional molecule of the acid chloride. The product is a cinnamate that, when decomposed with alcoholic potash, gives potassium cinnamate, and the potassium salt of diphenylpropionic acid.

III. Reactions with the Ethyl Anilide of Cinnamic Acid.

Cinnamyl Ethyl Anilide, $C_6H_5CH : CHCON(C_2H_5)C_6H_5$.—To prepare the ethyl anilide of cinnamic acid, pure, distilled cinnamyl chloride was gradually added to an excess of ethyl aniline. The reaction which took place in the cold was completed by warming for an hour on a water-bath. The resulting oil was poured into dilute hydrochloric acid, the insoluble portion dissolved in ether, and the ethereal solution washed with dilute hydrochloric acid and with a dilute solution of sodium carbonate. The ether, on evaporation, left a greenish-yellow oil that solidified on standing. The solid was purified by recrystallization from low-boiling ligroin. It may also be purified by solution in ether and precipitation with ligroin,

but has a strong tendency to separate from solution as an oil. From ligroin it crystallizes in large colorless prisms that melt at 74°. It is readily soluble in ether, alcohol, chloroform, and carbon bisulphide; moderately soluble in boiling ligroin. An analysis gave the following results:

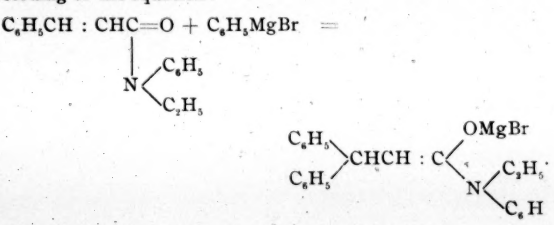
0.1280 gram substance gave 0.5409 gram CO_2 and 0.1117 gram H_2O.

	Calculated for $C_{17}H_{17}ON$.	Found.
C	81.28	81.05
H	6.77	6.82

Diphenylpropionethyl Anilide, $(C_6H_5)_2CH.CH_2CON\begin{matrix}C_2H_5\\C_6H_5\end{matrix}$.—When an ethereal solution of cinnamic acid ethyl anilide was added, drop by drop, to a solution of phenylmagnesium bromide, each drop produced a white precipitate, which rapidly disappeared on shaking, until the liquid contained almost 1 molecule of the anilide for each atom of magnesium that was used in the preparation of the magnesium compound. As soon as the precipitate no longer disappeared on shaking, the mixture was poured into iced hydrochloric acid, and the product of the reaction isolated in the usual way. The result was an oil that could not be obtained in solid form. The oil contained nitrogen, and the products of hydrolysis show that, for the most part at least, it was the ethyl anilide of β,β-diphenylpropionic acid.

For the purpose of hydrolysis, 20 grams of the oil were heated at 150°, for eight hours, with concentrated hydrochloric acid. The contents of the tube were then diluted with water and extracted with ether. The ether, on evaporation, left 12.5 grams of an acid that melted sharply at 150° after one recrystallization from dilute alcohol, and was β,β-diphenylpropionic acid. The aqueous solution from which the acid had been removed was evaporated to dryness, the green residue dissolved in water, the solution made alkaline with potassium hydroxide, and distilled in a current of steam. Ethyl aniline, boiling

at 195°, passed into the distillate. The 12.5 grams of acid correspond to 90 per cent of diphenylpropion ethyl anilide. At least 90 per cent of the original anilide, therefore, reacted according to the equation:



The magnesium compound that is formed has the same general properties as those magnesium compounds obtained from esters by the same reaction. When decomposed with water or acids the product is the ethyl anilide of a saturated acid. On treatment with bromine it gives a brom substitution-product of this anilide, as shown by the following experiment:

An ethereal solution of 25 grams of cinnamyl ethyl anilide was added to a solution of phenylmagnesium bromide, obtained by dissolving 2.6 grams of magnesium in 18 grams of brombenzene. After boiling the mixture for half an hour it was cooled in a freezing-mixture and treated with bromine that had been distilled from phosphorus pentoxide. The bromine was added very slowly, from a dropping-funnel, until the red color of the liquid showed a slight excess. The thick, pasty liquid obtained in this way was immediately poured into water. The ethereal layer was separated, washed with dilute sodium carbonate until colorless, and dried with sodium sulphate. On evaporating the ether, a solid separated in large, lustrous prisms. The substance was purified by recrystallization from alcohol until the melting-point remained constant at 178°. An analysis gave the following results:

0.1632 gram substance gave 0.4039 gram CO_2 and 0.0819 gram H_2O.

	Calculated for $C_{23}H_{22}ONBr$.	Found.
C	67.65	67.49
H	5.40	5.58

Diphenylbrompropion ethyl anilide crystallizes in large, colorless prisms. It is readily soluble in chloroform, acetone, and boiling alcohol; moderately in ether and cold alcohol; sparingly in ligroin.

Diphenylbrompropionic acid, $(C_6H_5)_2CH.CHBrCO_2H$, was obtained by hydrolyzing the ethyl anilide with concentrated hydrochloric acid in a sealed tube. It was purified by recrystallization from a mixture of ether and ligroin. The analysis gave the following results:

0.1485 gram substance gave 0.3203 gram CO_2 and 0.0601 gram H_2O.

	Calculated for $C_{15}H_{13}O_2N$.	Found.
C	59.01	58.81
H	4.26	4.50

The acid is readily soluble in alcohol and in ether, sparingly in ligroin, insoluble in water. It melts with decomposition at about 164°. When boiled with alcoholic potash it slowly loses hydrobromic acid and passes into β-phenylcinnamic acid. As this is the easiest way of getting β-substituted cinnamic acids, an effort was made to prepare the brom acid by direct bromination of diphenylcinnamic acid by the Hell-Volhard-Zelinsky method, but it was found that the acid bromide, which is formed intermediately, so easily undergoes internal condensation that the main product invariably is phenylhydrindone:

$$(C_6H_5)_2CHCH_2CO_2H \rightarrow (C_6H_5)_2CHCH_2COBr \rightarrow C_6H_4\begin{cases} \\ \end{cases}\!\!\begin{matrix} C_6H_5 \\ CHCH_2 \\ CO \end{matrix}.$$

β-Phenylcinnamic Acid, $(C_6H_5)_2C : CHCO_2H$.—An alcoholic solution containing 10 grams of diphenylbrompropionic acid was boiled for four hours with an excess of potassium hydroxide. The solution was poured into water, the alcohol removed

by distillation, and the aqueous solution concentrated on the water-bath and acidified. The solid acid that separated was free from bromine. The yield was good—7 grams instead of 7.3 grams calculated—and the product almost pure, as one recrystallization from aqueous alcohol gave a substance melting sharply at 142°. The analysis gave the following results:

0.1206 gram substance gave 0.3547 gram CO_2 and 0.0594 gram H_2O.

	Calculated for $C_{15}H_{12}O_2$.	Found.
C	80.35	80.25
H	5.35	5.50

β-Phenylcinnamic acid crystallizes in colorless needles. It is readily soluble in alcohol and in ether, moderately in boiling water, sparingly soluble in ligroin. It does not combine with bromine at ordinary temperatures, but instantly reduces cold solution of potassium permanganate. The products of oxidation are benzophenone, carbon dioxide, and water.

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August, 1904.

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND UNSATURATED COMPOUNDS.

III. REACTIONS WITH COMPOUNDS CONTAINING BROMINE.

BY E. P. KOHLER AND RUTH M. JOHNSTIN.

The principal object of the experiments described below was to ascertain to what extent the reactions considered in previous papers[1] are influenced by the presence of halogen atoms in the α-position. Incidentally we also studied the reaction between organic magnesium compounds and some dihalogen compounds obtained by the addition of bromine to α,β-unsaturated acids and α,β-unsaturated ketones.

We have found that the presence of a halogen atom in the α-position does not materially affect the primary reaction between organic magnesium derivatives and unsaturated com-

[1] This JOURNAL, **31**, 642; **33**, 21.

pounds. This is clear from the reactions of α-bromcinnamic ester, as illustrated by the following equations:

I. $C_6H_5CH : \underset{\underset{Br}{|}}{C}COOC_2H_5 + C_6H_5MgBr =$

$$(C_6H_5)_2CH.\underset{\underset{Br}{|}}{C} : C\begin{matrix}OMgBr\\OC_2H_5\end{matrix}.$$

II. $C_6H_5CH : \underset{\underset{Br}{|}}{C}CO.OC_2H_5 + 2C_6H_5MgBr =$

$$(C_6H_5)_2CH.\underset{\underset{Br}{|}}{C} : C\begin{matrix}OMgBr\\C_6H_5\end{matrix}.$$

III. $C_6H_5CH : \underset{\underset{Br}{|}}{C}CO.OC_2H_5 + 2CH_3MgI =$

$$C_6H_5CH : \underset{\underset{Br}{|}}{C}-C\begin{matrix}CH_3\\OMgBr\\CH_3\end{matrix}.$$

All these reactions are exactly like the corresponding ones with cinnamic ester. The α-halogen atom, however, diminishes the tendency to form secondary products. With α,β-unsaturated esters and α,β-unsaturated ketones that have hydrogen in the α-position, secondary reactions invariably take place unless the magnesium compound is in large excess and the reaction is carried out in a freezing-mixture. With α-brom substitution-products of these substances the reactions can be carried out at the ordinary temperature, and, if the magnesium compound is in sufficient excess, even at the boiling-point of ether, without fear of secondary products.

It will be seen that we regard brombenzalacetophenone as an α-substitution-product although, hitherto, it has always been regarded as a β-bromketone. The substance was first made by Wislicenus and Schmidt,[1] by eliminating 1 molecule

[1] Ann. Chem. (Liebig), **308**, 219.

of hydrobromic acid from benzalacetophenone bromide. This reaction would certainly be expected to give an α-bromketone, because in all cases in which hydrobromic acid has been eliminated from an α,β-dibrom aldehyde, acid, or ester, the result has been an α-brom derivative. Wislicenus and Schmidt give no reasons for assuming a different result in the case of benzalacetophenone bromide, but their formula was evidently based on the following transformation. By boiling the bromide with alcoholic potash they obtained dibenzoylmethane and a substance which they regarded as either an enol modification of ordinary dibenzoylmethane or else a stereoisomer of that substance, which may itself be an enol modification. Assuming that these compounds were obtained as a result of direct replacement of bromine, they represented the reaction by the equation :

$$C_6H_5CBr : CHCOC_6H_5 + KOH = C_6H_5C(OH) : CHCOC_6H_5 \rightarrow C_6H_5COCH_2COC_6H_5.$$

Quite recently Ruhemann and Watson[1] have found that the substance obtained by the action of potassium hydroxide on brombenzalacetophenone does not have the composition of dibenzoylmethane, but that of an ethoxyl compound containing ethoxyl in place of bromine. Ruhemann and Watson retain the earlier formula for the bromketone and assume that the ethoxyl compound is formed either by direct replacement of bromine, or by preliminary loss of hydrobromic acid and subsequent addition of alcohol to the resulting acetylene ketone. There can be no doubt that the ethoxyl compound is a β-substitution-product of benzalacetophenone, but neither this nor any other reaction that involves the elimination of the bromine atom can be used to determine the structure of the brom ketone. It is well known that in compounds having halogen in combination with doubly-linked carbon it is easier to eliminate the halogen as a halogen acid than to replace it. It seems probable, therefore, that in all transformations of these substances in which the halogen is apparently substituted, the

[1] J. Chem. Soc., **85**, 456.

product that is obtained is, in reality, the result of addition to an acetylene compound, formed by loss of halogen acid from the ethylene derivative. In accordance with a well-known rule, this product will always be a β-derivative. Moreover, Moureu and Brachin[1] have found that, in the presence of alkalies, acetylene ketones readily combine with alcohols to form β-alkoxyl derivatives of ethylene ketones.

Our evidence as to the structure of brombenzalacetophenone seems conclusive. Phenylmagnesium bromide combines with α-bromcinnamic ester to form a magnesium compound which, when decomposed with water, gives diphenylbrompropiophenone, in which the bromine must be in the α-position. The same bromketone is obtained when the addition-product of phenylmagnesium bromide and brombenzalacetophenone is decomposed with water. The bromine in brombenzalacetophenone must, therefore, also be in the α-position.

The experiments with dihalogen compounds were made in the hope that it might be possible to get unsaturated tertiary alcohols, like diphenylstyrilcarbinol, indirectly, by first making the corresponding dihalogen compounds and subsequently removing bromine. It was found, however, that the magnesium compounds invariably eliminate either hydrobromic acid or bromine and subsequently combine, in the usual way, with the resulting unsaturated compounds. Two typical reactions are illustrated by the following equations:

$$C_6H_5CHBrCHBrCO.OC_2H_5 + 3C_6H_5MgBr = (C_6H_5)_2CH{-}CH : C\begin{matrix}OMgBr\\OC_2H_5\end{matrix} + C_6H_5.C_6H_5 + 2MgBr_2;$$

$$C_6H_5CHBrCHBrCOC_6H_5 + 2C_6H_5MgBr = (C_6H_5)_2CH{-}CBr : C\begin{matrix}OMgBr\\C_6H_5\end{matrix} + C_6H_6 + MgBr_2.$$

The unsaturated magnesium compound is formed even when the ketone contains but one halogen atom:

[1] Chem. Ztg., **28**, 731.

$$(C_6H_5)_2CH.CHBrCOC_6H_5 + 2C_6H_5MgBr = (C_6H_5)_2CHCH : C\begin{matrix}OMgBr \\ C_6H_5\end{matrix} + C_6H_5.C_6H_5 + MgBr_2.$$

EXPERIMENTAL.

I. Reactions with Unsaturated Compounds.

Phenylmagnesium Bromide and Ethyl α-Bromcinnamate.—An ethereal solution of 27 grams of the ester was added, gradually, to a solution of phenylmagnesium bromide, obtained by dissolving 5 grams of magnesium in 33 grams of brombenzene and 100 grams of ether. As soon as the yellow precipitate that first formed had completely disappeared the liquid was poured into ice-water and the product separated in the usual way. On evaporating the ether, nearly one-third of the product separated as a solid; the rest remained liquid even when cooled in a freezing-mixture. The solid was purified by solution in chloroform and precipitation with absolute alcohol. It melted at 163°, and was found to be the same diphenylbrompropiophenone that had previously been obtained by treating benzalacetophenone with phenylmagnesium bromide and bromine.[1]

The liquid containing the rest of the product was boiled for several hours with alcoholic potash. After evaporating the alcohol there remained a mixture of potassium bromide and potassium salts of organic acids that was almost completely soluble in water. The water solution was first extracted with ether to remove a small quantity of colored substances, then acidified with dilute acid. The organic acids were precipitated as an oil that solidified almost immediately. The solid was evidently a mixture of low- and high-melting acids. By fractional crystallization from water it was ultimately separated into benzoic acid, melting at 124°, and β-phenylcinnamic acid, melting at 155°. The nature of the latter acid was established by analysis and by oxidation. The analysis gave the following results:

0.1097 gram substance gave 0.3225 gram CO_2 and 0.0540 gram H_2O.

[1] This JOURNAL, 31, 652.

	Calculated for $C_{15}H_{12}O_2$.	Found.
C	80.35	80.54
H	5.35	5.60

The acid reduced alkaline permanganate solution in the cold, being oxidized to benzophenone, carbon dioxide and water.

The products obtained from the reaction are accounted for as follows : A part of the ester (about 70 per cent) combines directly with phenylmagnesium bromide. When the resulting magnesium compound is decomposed with water it gives α-brom-β,β-diphenylpropionic ester ; on boiling with alcoholic potash this passes into β-phenylcinnamic acid by hydrolysis and loss of hydrobromic acid. The rest of the ester reacts with phenylmagnesium bromide to form brombenzalacetophenone, which immediately combines with a second molecule of the bromide ; when the resulting magnesium compound is decomposed with water it forms α-brom-β,β-diphenylpropiophenone.

Methylmagnesium Iodide and Ethyl α-Bromcinnamate.—The reaction was carried out like that with phenylmagnesium bromide. The oily product contained no ester because no alcohol was obtained by boiling it with concentrated aqueous potassium hydroxide. It was slowly decomposed by boiling alcoholic potash, the products being potassium bromide, potassium benzoate, and a gum. The nature of the product was established by oxidation. A dilute solution of potassium permanganate was slowly added to the oil suspended in ice-water. As soon as the permanganate was no longer decolorized as fast as added, the liquid was distilled in a current of steam. The distillate contained acetone, because it gave dibenzalacetone when allowed to stand with benzaldehyde and a few drops of sodium hydroxide. From the residue left in the distilling flask we obtained benzoic acid and a small quantity of a very soluble, low-melting acid, which could not be identified with certainty, but which was probably oxyisobutyric acid. These oxidation-products indicate that the main product of the reaction was a tertiary alcohol :

$$C_6H_5CH : CBrCOOC_2H_5 + 2CH_3MgI + H_2O =$$

$$C_6H_5CH : CBrC\begin{matrix}\diagup CH_3 \\ -OH \\ \diagdown CH_3\end{matrix} + Mg\begin{matrix}\diagup OC_2H_5 \\ \diagdown I\end{matrix} + Mg\begin{matrix}\diagup OH \\ \diagdown I\end{matrix}.$$

Phenylmagnesium Bromide and α-Brombenzalacetophenone.— An ethereal solution of 28 grams of the ketone was added to a solution obtained by dissolving 5 grams of magnesium in 33 grams of brombenzene mixed with absolute ether. The reaction was carried out at the temperature of boiling ether. The yellow precipitate that separated immediately redissolved and the solution was poured into ice-water as soon as all the ketone had been added. Almost the entire product was deposited from the ether as a crystalline solid. The remainder was obtained by evaporating the residue on the water-bath. After one recrystallization from acetone the compound melted at 163°, the melting-point of pure α-brom-β,β-diphenylpropiophenone. The reaction was a perfectly clean one. The yield was 35 grams of pure bromdiphenylpropiophenone instead of 36.6 grams calculated.

Phenylbenzalacetophenone, $(C_6H_5)_2C : CHCOC_6H_5$. — When bromdiphenylpropiophenone is boiled with alcoholic potash it slowly loses hydrobromic acid. Twenty-four grams of the ketone were boiled with a solution of 3.5 grams of potassium hydroxide in absolute alcohol. The solution soon became bright yellow in color and potassium bromide separated on the walls of the flask. After boiling for six hours the alcohol was removed by distillation and the residue poured into water. The heavy oil, that remained after the removal of potassium bromide, was dissolved in ether, the ethereal solution dried with sodium sulphate, and the ether evaporated. The product again separated as an oil but this solidified on standing. The yellow solid was recrystallized from alcohol until the melting-point remained constant at 92°. An analysis gave the following results :

0.2011 gram substance gave 0.6534 gram CO_2 and 0.1045 gram H_2O.

	Calculated for $C_{21}H_{16}O$.	Found.
C	88.70	88.61
H	5.61	5.77

The ketone crystallizes from alcohol in large, lemon-yellow prisms. It is readily soluble in alcohol and in ether, slightly soluble in ligroin. The solution in concentrated sulphuric acid is yellow at first, but rapidly turns to a deep red color. Water reprecipitates the original substance. The structure of the compound was established by oxidation. For this purpose 4 grams of the ketone were suspended in dilute solution of sodium carbonate, contained in a distilling-flask that was connected with a condenser and a steam generator. From a dropping-funnel dilute solution of potassium permanganate was slowly added, while a rapid current of steam was passed through the boiling liquid. A colorless oil collected in the receiver. This solidified when touched with a crystal of benzophenone, the resulting solid melting at 56°, the melting-point of pure benzophenone. The contents of the distilling-flask were filtered, the filtrate evaporated to small volume and acidified. The solid that separated was benzoic acid and the liquid contained no other organic substance. The original compound was, therefore, β-phenylbenzalacetophenone :

$$(C_6H_5)_2C : CHCOC_6H_5 + 3O = (C_6H_5)_2CO + C_6H_5COOH + CO_2.$$

This is, doubtless, the easiest way of making ketones of this type.

II. Reactions with Saturated Halogen Compounds.

Phenylmagnesium Bromide and Stilbene Bromide.—Seventeen grams of finely powdered stilbene bromide were added to a solution obtained by dissolving 5 grams of magnesium in brombenzene and absolute ether. The substances react quietly at the ordinary temperature. After boiling for a short time to complete the reaction, the mixture was poured into dilute hydrochloric acid. The ethereal layer was separated and distilled in a current of steam as long as an oil, that solidified in the condenser, was carried over freely. The solid in the dis-

tillate was filtered off and crystallized from ligroin. It gave 7.8 grams of pure diphenyl. The residue in the distilling flask was recrystallized from alcohol and yielded 8 grams of stilbene. The reaction evidently takes place smoothly, according to the equation :

$$C_6H_5CHBrCHBrC_6H_5 + 2C_6H_5MgBr = C_6H_5CH : CHC_6H_5 + C_6H_5C_6H_5 + 2MgBr_2.$$

Phenylmagnesium Bromide and Dibromphenylpropionic Ester. —The reagents were brought together in ethereal solution, the temperature being kept below —15° in a freezing-mixture. After standing for five hours the product was treated in the usual way. The ethereal solution, on evaporation, left an oil that partially solidified on standing. The solid was found to be diphenylpropiophenone. The part of the product that did not solidify on standing was free from bromine. It was boiled with alcoholic potash for four hours. The residue, after removing the alcohol, was completely soluble in water. From this solution hydrochloric acid precipitated diphenylpropionic acid. Hence it is clear that the first reaction which occurs is exactly like that between phenylmagnesium bromide and stilbene bromide. The magnesium compound removes the two bromine atoms, leaving ethyl cinnamate. This subsequently reacts with more of the bromide and forms the magnesium compounds which give diphenylpropionic ester and diphenylpropiophenone when they are decomposed with water.

Phenylmagnesium Bromide and Benzalacetophenone Bromide. —The result of this reaction depends, to some extent, upon the temperature. In the first experiment the finely powdered ketone was added, very slowly, to a solution of the magnesium compound that was cooled in a freezing-mixture. On pouring the mixture into iced hydrochloric acid most of the product separated in colorless crystals. After purification, by recrystallization from acetone, the solid melted at 163°—the melting-point of bromdiphenylpropiophenone. The ethereal solution, containing the rest of the product, was evaporated in a current of air and the solid residue recrystallized from alcohol. It was

composed mainly of diphenylpropiophenone mixed with a small quantity of bromdiphenylpropiophenone. The reaction was also carried out at the temperature of boiling ether. The product thus obtained was free from bromine. It was composed of diphenyl, which was removed by distillation with steam, and diphenylpropiophenone. The reaction takes place smoothly, according to the equation :

$$C_6H_5CHBrCHBrCOC_6H_5 + 3C_6H_5MgBr = (C_6H_5)_2CHCH : C\begin{matrix}OMgBr\\C_6H_5\end{matrix} + (C_6H_5)_2 + 2MgBr_2.$$

The bromketone obtained when the substances react at low temperatures might be formed either by direct replacement of bromine by phenyl I., or by elimination of hydrobromic acid and subsequent addition II.

I. $$C_6H_5CHBrCHBrCOC_6H_5 + C_6H_5MgBr = (C_6H_5)_2CHCHBrCOC_6H_5 + MgBr_2.$$

II. $$C_6H_5CHBrCHBrCOC_6H_5 + 2C_6H_5MgBr = (C_6H_5)_2CHCBr : C\begin{matrix}OMgBr\\C_6H_5\end{matrix} + C_6H_6 + MgBr_2.$$

If the reaction had taken place as represented in I., the monobromketone would have been formed before the product was decomposed with water. This was not the case because no further reaction took place when a large excess (4 mols.) of phenylmagnesium bromide was added to the mixture, while, as shown below, bromdiphenylpropiophenone instantly reacts with phenylmagnesium bromide. The product must, therefore, be a magnesium compound that gives the bromketone when it is decomposed with water.

Benzalacetophenone Bromide and Naphthylmagnesium Bromide.—The solid ketone was added to an ethereal solution of α-naphthylmagnesium bromide that was cooled with running water. The product solidified when it was poured into iced hydrochloric acid and was purified by recrystallization from alcohol. An analysis gave the following results :

0.1899 gram substance gave 0.6213 gram CO_2 and 0.1024 gram H_2O.

	Calculated for $C_{28}H_{20}O$.	Found.
C	89.22	89.28
H	5.99	6.20

The solid is naphthylphenylpropiophenone because the same substance was obtained by treating benzalacetophenone with α-naphthylmagnesium bromide. The ketone is readily soluble in ether and in alcohol. It crystallizes in needles, melting at 121°.

α-Bromdiphenylpropiophenone and Phenylmagnesium Bromide.—Although bromdiphenylpropiophenone is almost insoluble in ether, it readily dissolves in an ethereal solution of phenylmagnesium bromide. The liquid becomes warm and in a short time all the bromketone disappears. The products of the reaction were separated in the usual way and were found to be diphenylpropiophenone and diphenyl. The final result is, therefore, the replacement of bromine by hydrogen. The diphenylpropiophenone is, however, not formed until the mixture is treated with water, because the result is the same when a large excess of phenylmagnesium bromide is used, while diphenylpropiophenone readily reacts with the bromide to form a tertiary alcohol. If the mixture is treated with benzoyl chloride before it is decomposed with water the product is benzoyltriphenylpropenol. This shows that the reaction takes place according to the equation:

$$(C_6H_5)_2CHCHBrCOC_6H_5 + 2C_6H_5MgBr =$$

$$(C_6H_5)_2CHCBr : C\begin{matrix}OMgBr \\ C_6H_5\end{matrix} + (C_6H_5)_2 + MgBr_2.$$

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A METHOD FOR THE DETERMINATION OF THE AFFINITIES OF ACIDS COLORIMETRICALLY, BY MEANS OF CERTAIN VEGETABLE COLORING MATTERS.

By J. H. Kastle.

The bleaching of colored flowers, such as the rose and red geranium, by means of sulphur dioxide, is one of the best known reactions of which the latter substance is capable, and it is a matter of common observation that flowers thus bleached frequently regain their original color, in part at least, if, after bleaching, they are allowed to stand for some time in contact with the air. The most obvious explanation of this phenomenon is that the sulphur dioxide, by its reducing action, produces a leuco-compound which is reoxidized on exposure to the air. It occurred to me that possibly these leuco-compounds, if really formed, could be used advantageously in measuring such oxidations as are usually brought about by the oxidases. Accordingly, several years ago, the attempt was made to employ an aqueous extract of the red geranium, that had been bleached by sulphur dioxide, as a reagent for detecting the presence of oxidizing ferments and roughly measuring their relative oxidizing powers. These earlier experiments led to no noteworthy results and after a time were discontinued. Recently the subject was taken up again in connection with some other work and it appeared that possibly the difficulties had arisen from the use of an insufficiently highly colored substance for the preparation of the leuco-compound. Accordingly, some new experiments were undertaken, using the red substance of the purple grape, the Ives Seedling variety. An aqueous extract of this was obtained by macerating the hulls of the ripe grape with water and boiling. After filtering, a dark purplish-red solution was obtained. On adding a very small amount of hydrochloric acid to this solution and shaking with zinc dust, it was speedily decolorized. On standing in a loosely stoppered test-tube the upper layers of liquid gradually regained their color. As in the case of the coloring matter of the geranium, this seemed to indicate that, in the presence of

small amounts of acid, zinc dust can reduce the red coloring matter of the grape to the corresponding leuco-compound, which is again oxidized on exposure to the air. In order to determine whether this colorless solution could be oxidized by means of oxidizing ferments, small amounts of the solution were mixed with an active extract of *lepiota Americana*, a fungus which I have found to contain a very powerful and relatively stable oxidase. It was observed that the boiled extract of the fungus produced the same amount of colored substance as its active preparations. It was also found that active extracts of the fungus, after mixing with the solution of the leuco-compound obtained from the grape, failed to give the guaiacum reaction. It was evident, therefore, that the production of the red coloring matter of the grape from the leuco-compound was not the result of oxidation, but was in some way dependent on the degree of acidity of the solution, as it was found that the intensity of the red coloration could always be greatly increased by the addition of small amounts of hydrochloric acid. A comparison of hydrochloric and acetic acids, of the same concentration, showed that, whereas the tube containing the hydrochloric acid became deep wine-red in color, that containing an equal amount of acetic acid remained practically colorless, or at most showed only faint traces of pink. This difference in the conduct of these two acids proved so striking as to suggest that the solution of the leuco-compound obtained from the purple grape could be employed in determining the affinities of acids colorimetrically.

Preparation of the Reagent.

The best method of preparing the leuco-reagent consists in macerating the hulls of the grape with water, boiling, and filtering. In order to further clarify the filtrate a small amount of a solution of egg albumen is added. After boiling and filtering a second time a perfectly clear, dark plum-red solution is obtained. A rapid current of sulphur dioxide is then passed into this liquid, which quickly becomes lighter in color, until, finally, a light salmon-pink solution is obtained which is boiled to remove the excess of sulphur dioxide. During the boiling

the color darkens but fades on cooling, leaving the solution of a very faint pink tint; a little toluene is added and the liquid protected from air. Thus prepared the solutions are quite stable and may be kept for weeks and probably longer, without undergoing change.

In studying the effect of various acids on the reagent, 1 cc. of the N/10 acid was mixed with 1 cc. of the reagent. Acids having an affinity approximately equal to that of hydrochloric acid, gave immediately a dark wine-red color, whereas weaker acids yielded a pink one, which varied in depth and tint according to the affinity of the acid employed. A comparison of the color produced with the acid under investigation and that obtained with hydrochloric, oxalic, formic and acetic acids, as standards of comparison, readily permitted the determination of its relative affinity. The color comparisons were made in small, thin-wall test-tubes of the same internal diameter. Heretofore all measurements have been made on N/10 acids, except in one or two instances.

Hydrochloric, benzene sulphonic, sulphuric, oxalic, formic, acetic, and butyric acids were the first to be tested. On mixing 1 cc. of each of these acids, in N/10 solution, with 1 cc. of the reagent the following results were obtained:

Acid.	Color of the solution.
Hydrochloric	Dark wine-red
Benzene sulphonic	" "
Sulphuric	" " lighter than two preceding
Oxalic	Dark pink, lighter than sulphuric
Formic	Pink, lighter than oxalic
Acetic	Very light pink
Butyric	" " "
Water	Trace of pink

At this dilution and with these amounts of substances, acetic and butyric acids and water gave very nearly the same shade of color, but it was very easy to distinguish formic acid from any of these and to see that the acids stood in the following order of strength:

Hydrochloric = benzene sulphonic>sulphuric>oxalic>
formic>acetic = butyric.

The reagent possesses the further advantage that the colors produced with acids are permanent, showing no tendency to fade but persisting for hours and even days, unchanged.

Succinic, Malic and Tartaric Acids.

A comparison was made of the three related acids, succinic, malic and tartaric, in the manner described above:

Acid.	Color of the solution.
Tartaric	Deep pink
Formic	Pink
Malic	Light pink
Succinic	Very light pink

After standing twenty-four hours the color of the several tubes was essentially unchanged. Formic acid was included in this series for the sake of comparison. It is evident that the following relation obtains as to the order of strength of these acids:

Tartaric>formic>malic>succinic.

Propionic and Lactic Acids.

Propionic and lactic acids were next compared in the same manner:

Acid.	Color of the solution.
Lactic	Light pink, lighter than formic, darker than malic
Propionic	Very light pink, lighter than succinic

From the color comparison in the case of these two acids there can be no doubt that lactic acid is considerably stronger than propionic, and that the latter belongs to the class of very weak acids, such as acetic and butyric.

Acetic, Monochloracetic, and Trichloracetic Acids.

Acetic, monochloracetic, and trichloracetic were the next acids compared, using hydrochloric, oxalic and formic acids as standards:

Acid.	Color of the solution.
Hydrochloric	Dark wine-red
Trichloracetic	Wine-red, lighter than hydrochloric
Oxalic	Deep pink
Monochloracetic	Pink, lighter than oxalic
Formic	" " " monochloracetic
Acetic	Very light pink

These acids therefore stand in the following order of affinity :

Hydrochloric>trichloracetic>oxalic>monochloracetic>formic>acetic.

Nitric, Hydrobromic, Iodic, and p-Nitrotoluene Sulphonic Acids.

These acids were compared with hydrochloric :

Acid.	Color of the solution.
Hydrochloric	Dark wine-red
Nitric	" "
Hydrobromic	" "
p-Nitrotoluene sulphonic	" "
Iodic	Yellow

It will be observed that nitric, hydrobromic, and *p*-nitrotoluene sulphonic acids are equal to hydrochloric acid in their affinity. The yellow color produced by the iodic acid is due to the liberation of iodine by the action, on the iodic acid, of the small amount of sulphur dioxide remaining in the reagent. Its exceptional conduct is thus readily accounted for.

Citric and Meconic Acids.

Citric and meconic acids were compared, using hydrochloric, formic, and acetic as standards :

Acid.	Color of the solution.
Citric	Pink
Formic	"
Acetic	Very light pink

It is evident, therefore, that citric acid is stronger than acetic and that it is equal to, or possibly a little stronger than formic acid.

It was found impossible to prepare a N/10 solution of meconic acid in the cold, owing to its sparing solubility. Accord-

ingly, a saturated solution of the acid, in the cold, was prepared and titrated with N/10 sodium hydroxide. Ten cc. of the solution required 6.35 cc. N/10 sodium hydroxide for neutralization. In order to determine its effect on the reagent and to compare it wth hydrochloric acid, two tubes were set up. Tube 1 contained 1 cc. of the solution of meconic acid and 1 cc. of the reagent. Tube 2 contained 0.635 cc. N/10 hydrochloric acid, 0.365 cc. of water, and 1 cc of the reagent. Both tubes at once developed a dark wine-red color; the result of two comparisons showed the tube containing the meconic acid to be distinctly darker in color than that containing the hydrochloric acid. Ostwald states that meconic acid is conspicuous by its great strength. It is the strongest of all acids that consist only of carbon, hydrogen, and oxygen, and approaches very near to sulphuric acid in degree of affinity.

The Affinity of Acid Ethyl p-Nitrosulphobenzoate, $C_6H_3\begin{cases}COOC_2H_5\ (1)\\ SO_2OH\ (2)\\ NO_2\ (4)\end{cases}$.—This compound was prepared by me several years ago and was described as a strong acid.[1] So far as I am aware, no one has ever attempted to determine its affinity. If the compound owes its acidity to the existence of the sulphonic acid group in its molecule, it should have an affinity practically equal to that of hydrochloric acid, because the other groups in the compound are either inert or of an electronegative character. It seemed of interest to determine the affinity of this acid by means of the new reagent. A solution of the acid, of such concentration that 10 cc. required 6.15 cc. of N/10 sodium hydroxide to neutralize, it was compared with hydrochloric acid as before.

Tube No. 1 contained 1 cc. of the solution of the acid ester of *p*-nitrosulphobenzoic acid, and 1 cc. of the reagent.

Tube No. 2 contained 0.615 cc. of N/10 hydrochloric acid, 0.385 cc. of water, and 1 cc. of the reagent.

Both tubes developed a wine-red color at once, of the same depth and tint. It would seem, therefore, that the acid ester

[1] This JOURNAL, 11, 190 (1889).

of *p*-nitrosulphobenzoic acid is as strong an acid as hydrochloric, a conclusion which is in harmony with the present view regarding the constitution of the former substance.

In the following table the acids here studied have been arranged in order of their strength, as determined by Ostwald's methods, and as determined colorimetrically according to the process here under consideration. The agreement is certainly as close as could be desired when we consider the great diversity of the means employed.

Table I.—Acids Arranged in Order of Their Strength.

According to Ostwald's methods.	Colorimetrically.
Hydrochloric	Hydrochloric
(Nitric)[1]	(Nitric)
(Hydrobromic)	(Hydrobromic)
(Benzene sulphonic)	(Benzene sulphonic)
	(Meconic)
	(*p*-Nitrotoluenesulphonic)
	(Acid ethyl *p*-Nitrosulphobenzoate)
Trichloracetic[2],	Trichloracetic
Sulphuric	(Sulphuric)
Meconic	
Oxalic	Oxalic
Monochloracetic	Monochloracetic
Tartaric	Tartaric
Citric	Citric
Formic	Formic
Malic	Lactic[3]
Lactic	Malic
Succinic	Succinic
Acetic	Acetic
Propionic	(Propionic)
Butyric	(Butyric)

Hitherto it has not been found possible to recognize the difference in strength between the very weak acids, such as

[1] The sign of parenthesis enclosing the names of certain of the acids is intended to signify that the acids so enclosed have the same affinity as the acid immediately preceding.

[2] According to one of Ostwald's methods trichloracetic acid is weaker than sulphuric, whereas according to two of them it is stronger.

[3] According to one of Ostwald's methods lactic acid is stronger than malic, whereas according to two of them it is weaker.

acetic, propionic, and butyric, by this colorimetric method; however, these differences are only slight. By varying the concentration it may prove possible to exhibit them.

Other Vegetable Coloring Matters as Indicators of the Degree of Acidity.

The following plants have been examined for coloring matters similar to that of the purple grape: The red-leaved achyranthes, the flower of the scarlet geranium, the flower of the purple petunia, the beet (*beta vulgaris*), poke berries (*phytolacca decandra*), the wild grape (*vitis vulpina*), the purple morning glory (*ipomæa purpurea*), the scarlet sage (*salvia fulgens*), and the cultivated red rose.

Some of the flowers of the red geranium were crushed with water and the mixture boiled and filtered. The filtrate was found to have a dull rose-red color. It was then saturated with sulphur dioxide, after which a small quantity of a solution of egg albumen was added and the liquid boiled to expel the excess of sulphur dioxide and coagulate the albumen. A clear, practically colorless solution was thus obtained. With N/10 solutions of the strong acids, such as hydrochloric, hydrobromic and nitric, this solution gave, at first, delicate shades of pink, which finally changed to orange-yellow. Acids of the strength of oxalic gave a decided salmon-pink, formic acid a very faint pink color and acetic acid no color at all. Ten acids gave the following results:

Acids.	Color of the solution.
Hydrochloric	Orange-yellow
Hydrobromic	" "
Nitric	" "
Benzene sulphonic	" "
Sulphuric	Orange-yellow, with pink tint
Meconic,	Orange-yellow, with salmon-pink tint
Oxalic	Salmon-pink
Formic	Faint pink
Acetic	Very faint pink
Butyric	Colorless

We should, therefore, have to arrange these acids in the following order of strength :

Hydrochloric = hydrobromic = nitric = benzenesulphonic > sulphuric > meconic > oxalic > formic > acetic > butyric.

The effect of heat is to intensify the color produced by weak acids on this solution, as seen from the following :

Acid.	Color of the solution. Ordinary temperature.	100° C.
Hydrochloric	Orange-yellow	Orange-yellow
Formic	Light pink	Salmon-pink
Butyric	Colorless	Pink

It will be observed that the change produced by heat is greater for weak acids, such as formic and butyric, than it is for strong ones, such as hydrochloric. On cooling, the reverse change occurs, that is, the solutions tend to regain their original color. This reverse change, however, is incomplete, because the solutions that have once been heated are, on cooling, always a little darker than they were before heating. After heating and standing six hours, butyric acid, for example, showed a very faint pink color, whereas in the cold the solution is colorless.

Some experiments were next tried with the purple petunia. The flowers of this plant are deep plum-red in color. By maceration with water they gave a deep purplish-red solution which faded considerably on boiling, so that finally a magenta-red liquid was obtained. Sulphur dioxide rapidly changed the color to a pink and after boiling to remove the excess of gas and filtering, a yellow solution was obtained. With N/10 solutions of the strong acids, such as hydrochloric, nitric, etc., this liquid gave a faint pink coloration ; with the weaker ones, such as formic and acetic, no change of color was observable. On heating the solutions containing the strong acids, the color darkened rapidly, finally becoming deep rose-red. Oxalic acid also produced a rose-red color, lighter than that with hydrochloric acid. The solution containing formic acid developed a pink color, while the tubes containing acetic acid and water remained colorless, even after heating. On cooling, the solutions containing hydrochloric, nitric and hydrobromic acids

became deep pink, that one with oxalic acid lighter pink and the formic acid colorless. It is evident, therefore, that the coloring matter in the colored petunia can be employed, like that in the purple grape and the red geranium, for the determination of the affinities of acids colorimetrically. The acids tested with this reagent can be arranged in the following order of strength:

Hydrochloric = hydrobromic = nitric > oxalic > formic > acetic.

The coloring matter in the flowers of the scarlet sage (*salvia fulgens*) was next tried, the flowers being macerated with water and boiled. Unfortunately, a good deal of the color was lost on boiling. After boiling and filtering, the solution was found to be purplish-red in color. It was saturated with sulphur dioxide and boiled to remove the excess of the gas. While hot it had an orange-yellow color, which, on cooling, became light-yellow. In its conduct toward acids this vegetable coloring matter was found to be very similar to that present in the red geranium. The color of the flowers of these two plants is very much alike. The following results were obtained with some of the N/10 acids:

Acid.	Color of solution, cold.	Color of solution, hot.
Hydrochloric	Salmon-pink	Orange-yellow
Hydrobromic	"	"
Nitric	"	"
Acetic	Colorless	Pink
Water	"	Very light pink

Meconic acid was compared with hydrochloric acid in the manner already described on page 50, with the following result:

Acid.	Color of the solution.
Hydrochloric	Salmon-pink
Meconic	"

In the order of their strength, therefore, these acids should be arranged as follows:

Hydrochloric = hydrobromic = nitric = meconic > acetic.

A solution of the coloring matter in the wild grape (*vitis*

vulpina), prepared and bleached with sulphur dioxide in the manner already described, was found to conduct itself towards acids in precisely the same way as the cultivated variety. With the strong acids, such as hydrochloric, nitric, etc., it gave beautiful wine-red solutions, with the weaker ones, such as formic and acetic, delicate shades of pink.

With poke berries, the purple beet, and the flowers of the purple morning glory no satisfactory results were obtained, doubtless for the reason that it was found difficult, or in some cases impossible, to bleach the coloring matters of these plants by means of sulphur dioxide. After saturating the solution with sulphur dioxide, prolonged boiling removes the color of the purple beet, with the result, however, that the coloring matter seems to be permanently destroyed. On the other hand, the coloring matters of the poke berry and the purple morning glory, while quite unstable, do not seem capable of being bleached by sulphur dioxide.

Interesting results have been obtained with the cultivated variety of the red rose. The coloring matter was extracted with cold water and the solution saturated with sulphur dioxide. A slight yellowish-pink liquid was thus obtained. With N/10 acids this solution gave the following colors:

Acid.	Color of solution, hot.	Color of solution, cold.
Hydrochloric	Deep reddish-orange	Rose-pink
Hydrobromic	.....	"
Nitric	.....	"
Benzene sulphonic	.....	" darker than hydrochloric
Meconic	.....	Rose-pink, lighter than hydrochloric
Oxalic	.....	Very faint pink
Acetic	Pink	Colorless
Water	"	"

On cooling the hot solutions containing the acetic acid and water they became colorless and the hot solution of hydrochloric acid, which was deep reddish-orange, became rose-pink, deeper in color, however, than the solution that had remained in the cold.

Some of the solution of the coloring matter of the red rose, which had been extracted with cold water and bleached with sulphur dioxide, was boiled for a short time to expel the excess of sulphur dioxide. On cooling, the liquid was found to have a very slight yellowish color and when mixed with an equal volume of N/10 hydrochloric acid it developed a deep rose-red color at once, much deeper in fact than had been obtained with the solution before it was boiled. With the boiled solution the following results were obtained:

Acid.	Color of the solution, cold.
Hydrochloric	Deep rose-red, tending to orange
Nitric	" " " " "
Oxalic	" rose-pink, much lighter than hydrochloric
Formic	Very faint salmon-pink
Acetic	Colorless

The difference between acids equal or superior to oxalic in strength and those equal or inferior to formic is certainly distinctly brought out in these experiments.

The coloring matter of the red rose was found to dissolve readily in 95 per cent alcohol even in the cold. A small amount of this solution was allowed to evaporate spontaneously in the air, and the residue dissolved in a small quantity of water. On adding a drop or two of N/10 hydrochloric acid it became deep orange-red and much darker than it was originally. This suggested that possibly a solution of the coloring-matter of the red rose could be employed to determine the strength of acids colorimetrically, without previously bleaching with sulphur dioxide. Accordingly, an equal volume of water was added to an alcoholic solution of the coloring matter of the red rose and the mixture heated on the water-bath until all of the alcohol was removed. The aqueous solution was diluted with distilled water and divided into three portions. These were employed as follows:

1. One was boiled, with the addition of a small amount of animal charcoal, and filtered. The solution thus obtained was slightly yellowish and gave the following results with water and acids:

Acid.	Color of the solution.
Hydrochloric	Deep rose-pink
Acetic	Faint pink
Water	Colorless

2. The second portion was treated with a small amount of animal charcoal in the cold and filtered. It was found possible to remove the red color even in this way, a slightly yellowish solution resulting, which gave the following results with water and acids:

Acid.	Color of the solution.
Hydrochloric	Deep rose-pink
Acetic	Faint pink
Water	Colorless

3. The third portion of the solution was simply diluted with water until it had only a faint yellowish-pink color. With water and acids it gave the following results:

Acid.	Color of the solution.
Hydrochloric	Deep rose-pink
Oxalic	" " (only a little lighter than hydrochloric)
Formic	Light pink
Acetic	Very faint pink
Water	Colorless

From a superficial consideration of these results one might be inclined to believe that dilute solutions of the plant coloring matter could be employed directly in determining the strength of acids, without previously bleaching with sulphur dioxide. It should be observed, however, that although the color of such liquids is greatly increased by the addition of an acid and although a much deeper coloration is produced by a strong acid than by a weak one, the reagent is lacking in sensitiveness. For example, it will be seen from the results under 3 that oxalic acid produced very nearly as intense a coloration as hydrochloric acid. On the other hand, if we employ a solution of the coloring matter of the red rose that has been bleached with sulphur dioxide, the difference between hydrochloric and oxalic acid is readily perceptible, as will be seen from the results recorded on page 56.

The same is true of the purple coloring matter of the grape, namely, that the color of its solutions is markedly intensified by the addition of an acid. An aqueous extract of the hulls of the purple grape, that had been diluted until it had only a faint pink color, gave the following results on the addition of N/10 acids:

Acid.	Color of the solution.
Hydrochloric	Deep pink
Oxalic	" " (only a little lighter than hydrochloric)
Formic, tartaric, and lactic	Light pink, and not distinguishable one from the other
Acetic	Very faint pink
Water	" " " (lighter than acetic acid)

Here, again, we see that the solution lacks delicacy as compared with the solutions of the coloring matter that have been bleached with sulphur dioxide. It will be observed, therefore, that, by means of certain of the vegetable coloring matters which have been bleached by sulphur dioxide, it is possible to determine the relative affinity of acids colorimetrically, with the greatest ease and rapidity, and that the color changes are such as to render the method a beautiful one for the purposes of chemical demonstration. As to the mechanism of the reaction upon which the method is based but little is known at present. Acids are essential to the development of the color of certain dye-stuffs, such as those of the rosaniline type. If acids are required to produce the colored substance from an antecedent chromogen it is but logical to conclude that, in certain cases at least, the quantity of the colored substance actually formed and existing in the solution of the dye, and hence the intensity of the color, would depend not only on the quantity of acid present but also on the degree of its ionization.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, KY., Sept., 1904.

ON DERIVATIVES OF FORMHYDROXAMIC ACID AND THE POSSIBLE EXISTENCE OF ESTERS OF FULMINIC ACID.

By H. C. Biddle.

The possible existence of esters of fulminic acid,

$$R—O—N=C,$$

is of interest not only on account of the isomerism of these bodies with the alkyl isocyanates, but also because of their presenting additional examples of bivalent carbon.

The extent to which the valence of an element may be varied by the nature of an attached radical is a subject of ever increasing importance. It would appear that the limits of such variation are somewhat wider than was anticipated a few years ago. The tetravalence of oxygen seems now to be established beyond dispute.[1] If the determination of the molecular complexity of a metal dissolved in mercury is a just criterion of its molecular aggregation,[2] the metal is apparently monatomic under such conditions, and the valence of the atoms for one another is consequently zero. The bivalence of carbon appears to obtain in such derivatives as carbon monoxide, the isonitriles[3] and the fulminates. In triphenylmethyl, Gomberg[4] has shown strong probability of the existence of trivalent carbon, and Thiele[5] would explain the mechanism of many reactions on the assumption of a residual affinity of the carbon atom, thus ascribing to the element a potential valence of five.

The similarity in structure between the isonitriles and the esters of fulminic acid would naturally lead us to expect a close resemblance in general behavior between these two classes of bodies. Like the former, the latter would probably be characterized by an "isonitrile" odor. Being unsaturated, they should exhibit an absorptive tendency toward such bodies as the halogens. On saponification they would probably yield formic acid and the α-alkylated hydroxylamines.

[1] Baeyer and Villiger: Ber. d. chem. Ges., **34**, 2679 (1901), and others; see Review, This JOURNAL, **27**, 311 (1902).

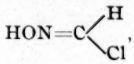
[2] Ramsay: J. Chem. Soc. (London), **55**, 521 (1889).

[3] Nef: Ann. Chem. (Liebig), **270**, 267 (1892); **280**, 291 (1894); **287**, 265 (1895).

[4] Ber. d. chem. Ges., **33**, 3150 (1900); **34**, 2726 (1901); etc.

[5] Ann. Chem. (Liebig), **306**, 87 (1899).

The synthesis of such a class of bodies as the fulminic esters seems not improbable, although their preparation by the action of alkyl iodides on silver or mercury fulminate is, apparently, not feasible.[1] The properties of formyl chloride oxime,

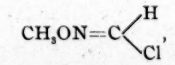


as described by Nef, suggest the possibility of eliminating hydrogen chloride from the alkyl derivatives of this body as a method for obtaining the alkyl fulminates. Some time ago, with this end in view, the benzyl, benzoyl, and acetyl derivatives of formyl chloride oxime were synthesized and their properties studied.[2]

Benzyl formyl chloride oxime is a body of great stability and boils, without decomposition, under atmospheric pressure, at about 210°. On treatment with alcoholic potash, however, the molecule is completely disrupted, there being formed, among other products, hydrochloric acid, ammonia, and benzyl alcohol. In this reaction there is not the slightest odor in any way resembling that of an isonitrile.

Acetyl formyl chloride oxime is a body of much less stability than the corresponding benzyl derivative. With silver nitrate it undergoes decomposition, yielding, among other products, silver fulminate.

With the thought that the methyl ester would probably afford more satisfactory results, a study of this derivative has been undertaken. Methyl formyl chloride oxime,



as I shall show later in this paper, is a body closely resembling the benzyl ester in stability. Its decomposition with caustic alkalies, under like conditions, appears to be less deep-seated than that of the latter. On treatment with potassium hydroxide it yields, apparently, minute quantities of a neutral, unsaturated

[1] Nef: Ann. Chem. (Liebig), **280**, 339 (1894).
[2] *Ibid.*, **310**, 1 (1899).

body, possessing a strong isonitrile-like odor, together with other products.

That the body in question is the fulminic ester,

$$CH_3—O—N=C,$$

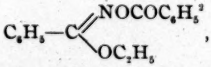
seems highly probable, though, unfortunately, the difficulty of preparing material, and the small quantity of substance obtained have thus far precluded its isolation and identification.

EXPERIMENTAL.

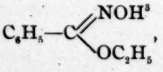
Synthesis of α-Methyl Hydroxylamine Hydrochloride, $CH_3ONH_2.HCl$.—The preparation, in quaniity, of the α-alkylated hydroxylamines of the aliphatic series presents a number of difficulties. The following process, however, while quite long and tedious, affords fair yields of the methyl derivative.

Hydroxylamine hydrochloride is converted into dibenzhydroxamic acid, according to the general method suggested by Lossen.[1] The product of the reaction is allowed to stand one to two days and is then filtered, without acidifying it, as directed by Lossen.

The crude acid is purified by washing with water, digesting with hydrochloric acid and again washing with water. The yield should at least equal 80 per cent of the theory (calculating from hydroxylamine hydrochloride used). When dry, the acid is dissolved in cold baryta water (0.5 molecule $Ba(OH)_2$), and is precipitated as silver salt by the addition of silver nitrate. From the silver salt are obtained, by successive steps, the ethyl ester of dibenzhydroxamic acid,

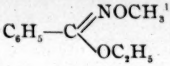


ethyl benzhydroxamic acid,



[1] Ann. Chem. (Liebig), **161**, 351 (1872).
[2] Eiseler: *Ibid.*, **175**, 326 (1875).
[3] Eiseler: *Ibid.*, **175**, 328 (1875); **205**, 285 (1880).

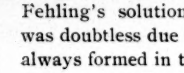
and the methyl ester of the latter,



Satisfactory results are secured by making use, in the different steps, of the crude products as they are obtained from the ether extracts, after distilling off the ether on the water-bath. On saponification with hydrochloric acid, the methyl ester of ethyl benzhydroxamic acid is readily decomposed into ethyl benzoate and methoxylamine hydrochloride.[2] The acid solution is evaporated to dryness on the water-bath and the crude salt purified by crystallizing it twice from alcohol and ether. From 250 grams of hydroxylamine hydrochloride 70 grams of α-methyl hydroxylamine hydrochloride are thus obtained, crystallizing in snow-white, hygroscopic leaflets, and melting at 148° to 149°.

α-Methyl hydroxylamine hydrochloride does not reduce Fehling's solution. The reducing action noted by Lossen[2] was doubtless due to the presence of the β-derivative, which is always formed in the above synthesis. As has been shown by Dunstan and Goulding,[3] the formation of β- with α-derivatives is a normal result when alkylating the aldoximes and ketoximes in the presence of sodium alcoholates.

The Methyl Ester of Formhydroxamic Acid,



.—As I have shown, the alkyl esters of formhydroxamic acid are readily obtained by heating formic acid with α-alkylated hydroxylamines.[4]

To 30 grams of α-methyl hydroxylamine hydrochloride, a concentrated solution of potassium hydroxide (1 to 2 molecules) is added and the mixture is slowly distilled into formic acid (99 per cent), the temperature of the distilling-bulb being eventually raised to 150°.

The formic acid solution is concentrated on the water-bath

[1] Lossen: Ann. Chem. (Liebig), **182**, 224 (1876); **281**, 216 (1894).
[2] Lossen and Zanni: *Ibid.*, **182**, 225 (1876).
[3] J. Chem. Soc. (London), **79**, 628 (1901).
[4] Ann. Chem. (Liebig), **310**, 9 (1899).

and is then distilled under diminished pressure. The main fraction is a colorless liquid which boils at 116° to 117° under 33 mm., at 123° to 124° under 45 mm., and at 126° to 127° under 50 mm. pressure. On standing for a short time, the liquid solidifies to a mass of colorless, prismatic crystals, melting at 38° to 39°.

On analysis the following results were obtained:

0.1952 gram substance gave 0.2284 gram CO_2 and 0.1197 gram H_2O.

0.1560 gram substance gave 25 cc. moist N at 13°.5 and 758 mm. pressure.

	Calculated for $C_2H_5O_2N$.	Found.
C	32.00	31.91
H	6.66	6.81
N	18.66	18.90

The methyl ester of formhydroxamic acid is a deliquescent substance, possessing a marked tendency to crystallize. By the action of hydrochloric acid it is decomposed into formic acid and α-methyl hydroxylamine hydrochloride. The ester is also dissociated in the presence of chlorplatinic acid, the orange-yellow plates of the platinum double salt of α-methyl hydroxylamine hydrochloride being formed.

0.1559 gram substance gave 0.0601 gram Pt.

	Calculated for $(CH_3ONH_2.HCl)_2PtCl_4$.	Found.
Pt	38.69	38.55

Silver Salt of the Methyl Ester of Formhydroxamic Acid.—This salt is prepared by the addition of silver nitrate to a solution of the ester, in the calculated amount of dilute caustic sodium hydroxide. It separates in snow-white leaflets, which undergo but little change when dried *in vacuo* over sulphuric acid.

0.2338 gram substance gave 0.1842 gram AgCl.

	Calculated for $C_2H_4O_2NAg$.	Found.
Ag	59.34	59.29

When heated, the silver salt is decomposed. It reacts in the cold with acetyl and benzoyl chlorides and with methyl and

ethyl iodide, yielding the corresponding acyl and alkyl derivatives.

Action of Phenyl Isocyanate on the Methyl Ester of Formhydroxamic Acid.—Phenyl isocyanate readily reacts with the methyl ester to form an addition-product. The clear solution, resulting from gently warming an equimolecular mixture of the two substances, soon solidifies to a crystalline mass. After standing until the odor of the isocyanate has disappeared, the solid is recrystallized from chloroform and ether and is thus obtained in colorless leaflets, which melt at 123° to 123°.5.

0.1971 gram gave 24.3 cc. of moist N at 11°.5 and 753.7 mm. pressure.

	Calculated for $C_9H_{10}O_2N_2$.	Found.
N	14.43	14.58

This addition-product is difficultly soluble in ether, alcohol, and hot water, insoluble in cold water, readily soluble in chloroform. Its constitution is probably that of a urea rather than that of a urethane, although this has not as yet been determined. The solution of this question is of some interest, as it would doubtless indicate whether the original ester is to be regarded as a derivative of formhydroxamic acid, $CH_3—O—NH—CH=O$, or of formhydroximic acid, $CH_3—O—N=CH—OH$.

Methyl Formyl Chloride Oxime, $CH_3—O—N=C\begin{matrix}H\\Cl\end{matrix}$. — As I have shown, benzyl formyl chloride oxime is formed by treating the benzyl ester of formhydroxamic acid with phosphorus pentachloride.[1] In like manner, methyl formyl chloride oxime may be obtained from the methyl ester of formhydroxamic acid.

Ten grams of the methyl ester of formhydroxamic acid are well cooled and treated slowly with 27.7 grams of phosphorus pentachloride (1 molecule). The reaction begins immediately, with evolution of hydrogen chloride. When the product has become a homogeneous yellow liquid, it is carefully

[1] Ann. Chem. (Liebig), **310**, 11 (1899).

distilled, the temperature of the distilling bulb not being allowed to rise above that of boiling water. As soon as no further liquid condenses in the receiver, the colorless distillate, consisting of phosphorus oxychloride and methyl formyl chloride oxime, is well cooled and treated with an equal volume of water, to decompose the oxychloride. A colorless liquid is thus obtained, which, after standing over night in contact with calcium carbonate and calcium chloride, is found to distil without decomposition at 68°.

0.1300 gram substance gave 0.2005 gram AgCl (Carius).

0.1656 gram substance gave 21 cc. of moist N at 11°.5 and 760 mm. pressure.

	Calculated for C_2H_4ONCl.	Found.
Cl	37.90	38.16
N	14.98	15.12

Methyl formyl chloride oxime is a volatile liquid, slightly soluble in water. It possesses an odor strikingly similar to that of chloroform. In stability it closely resembles its homologue, benzyl formyl chloride oxime. It is unaffected by aniline at the ordinary temperature, but by prolonged heating at 100°, it is slowly acted upon with the separation of aniline hydrochloride. It is not attacked by silver nitrate, but is immediately decomposed when brought in contact with potassium or sodium hydroxides. If the powdered alkali be carefully added to well cooled methyl formyl chloride oxime, or better to its solution in dry ether or ligroin, an intense and unmistakable *isonitrile-like* odor is immediately produced. That this odor is due to the formation of minute quantities of methyl fulminate, $CH_3—O—N=C$, seems highly probable from the following considerations:

An ethereal solution of methyl formyl chloride oxime is completely freed from chlorine by treatment with an excess of powdered potassium hydroxide. If the solution be kept cool, the isonitrile odor is unaccompanied by any ammoniacal odor or reaction. On longer standing in contact with the potassium hydroxide, however, an amine odor arises and the vapor becomes alkaline in reaction.

An unsaturated body appears to result from the action of potassium hydroxide on methyl formyl chloride oxime. A ligroin solution, prepared as above, instantly decolorizes a small amount of bromine with the separation of minute yellow drops. The ligroin used, methyl formyl chloride oxime, and the methyl ester of formhydroxamic acid do not immediately decolorize a small amount of bromine.

To determine the nature of the odorous body, a solution of methyl formyl chloride oxime in absolute ether was treated with powdered potassium hydroxide and allowed to stand until action was completed. Little, if any, gas is evolved. After evaporating off the ether, a minute quantity of liquid, possessing a strong isonitrile odor, distilled over at from 50° to 60° (approximate temperature). The liquid remaining in the distilling-bulb and constituting the chief reaction-product, soon lost all odor of isonitrile. It was freed from traces of ether by warming and passing a current of air through it. A nitrogen determination seemed to indicate the presence of the methyl ester of formhydroxamic acid, $CH_3—O—NH—CH=O$.

0.1292 gram substance gave 20.7 cc. moist N at 14°.5 and 754.4 mm. pressure.

	Calculated for $C_2H_5O_2N$.	Found.
N	18.66	18.73

An attempt to distil the supposed ester under diminished pressure led to the isolation of only a very small quantity of substance, the contents of the distilling-bulb were largely converted into a resin.

The limited supply of material has thus far precluded a further study of this reaction; it is possible that the substance is a condensation-product of methyl fulminate.

Although, in the above experiment, it may be assumed that there is a direct interchange between the chlorine of the methyl formyl chloride oxime and the hydroxyl of the potassium hydroxide, it seems highly probable that the primary product of the reaction is the fulminic ester, $CH_3—O—N=C$. This, being in the nascent condition, may polymerize, or, by the ab-

sorption of a trace of water, be converted, in part, into the methyl ester of formhydroxamic acid. A minute quantity of the fulminic ester escapes further change and gives rise to the phenomena noted above.

A further indication of the presence of methyl fulminate in these reactions is that derived from the interaction of α-methyl hydroxylamine hydrochloride, chloroform, and alcoholic potassium hydroxide. With care, the same characteristic isonitrile odor noted above is obtained. It seems difficult to explain this on the basis of any other than the following reaction:

$$CH_3ONH_2 + CHCl_3 + 3KOH \rightarrow CH_3—O—N=C + 3KCl + 3H_2O.$$

A continuation of the work will, it is hoped, lead to the definite isolation of the fulminic ester, or some of its addition-products.

UNIVERSITY OF CALIFORNIA,
BERKELEY, CAL.,
Aug. 23, 1904.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE REACTIONS OF SODIUM BENZHYDROL.

BY RAYMOND FOSS BACON.

An exhaustive study by Nef[1] of benzhydrol and its derivatives, benzhydrol ether, bromdiphenyl methane, benzilic acid, etc., has shown that these substances possess very low dissociating-points. The dissociation-product common to all of them, diphenylmethylene, is not, however, capable of isolation as such. Similar results have been obtained by Miss Goldthwaite with the corresponding dibrom derivatives.[2] Since then it has been clearly proved by Nef[3] that all primary and secondary alcohols undergo analogous dissociation into water and alkylidenes, the sole difference being in the fact that the decomposition-point varies within considerable limits, 300° to 600°. We have, as yet, no accurate means for determining the exact percentage of water and ethylidene particles present, for

[1] Ann. Chem. (Liebig), **298**, 231–274.
[2] This JOURNAL, **30**, 447.
[3] Ann. Chem. (Liebig), **318**, 138–230.

instance, in alcohol or ether at the ordinary temperature. As ether decomposes at a temperature which is 50° lower than the decomposition-point of alcohol, 600°, ether must obviously contain more dissociated particles,

$$CH_3CH_2OCH_2CH_3 \rightleftarrows 2CH_3CH< + H_2O,$$

at the ordinary temperature than alcohol. This explains why ether burns slowly at ordinary temperatures, in the light, whereas this is not the case with alcohol, except in the presence of various catalytic agents, which have the effect of increasing most remarkably the percentage of the dissociated particles.

The experiments of Nef show further that if the hydroxyl hydrogen of an alcohol be replaced by a metal, such as Na, K, Ca, Ba, etc., the effect on the dissociating-point of the corresponding alcohol is most striking. The decomposition-point of sodium ethylate, for example, lies at 240°. Consequently there are, relatively, far more dissociated particles,

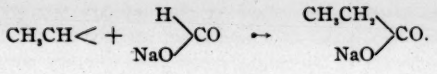
$$CH_3CH_2ONa \rightleftarrows CH_3CH< + H—ONa,$$

present at the ordinary temperature in sodium ethylate than in ether. Sodium ethylate, therefore, burns spontaneously, with considerable violence, in dry air or oxygen. The behavior of the metallic alcoholates of the aliphatic series has, in fact, been very thoroughly studied under the most varied conditions by Nef. He has found that they act as alkylating agents, and that they also decompose caustic alkalies with evolution of atomic hydrogen and can, therefore, act as reducing agents. Furthermore, it has been decisively established that the Geuther-Fröhlich reaction between carbonic oxide and sodium alcoholates is an alkylation phenomenon; *i. e.*, the reaction takes place in two stages, *viz.*, I.

$$CO + CH_3CH_2ONa \rightleftarrows CO + H—ONa + CH_3CH< \rightarrowtail$$

$$\rightarrowtail \begin{matrix} H \\ NaO \end{matrix}\!\!>\!CO + >CH—CH_3;$$

and then only to a slight extent according to II.



In these experiments, therefore, the yield of alkylated formic acid is usually exceedingly small. It was found in one instance to be very large, namely, with 1,3-decyl alcohol.[1] On the other hand, the yield in the case of the alkylation of acetic acid with sodium alcoholates was invariably large—15 to 30 per cent. As the alkylidene can also necessarily interact with the caustic alkali—the other dissociation-product—with evolution of hydrogen and the formation of an aldehyde, ketone, or fatty acid, it is obvious that alkylation by means of sodium alcoholates can never take place quantitatively.[2]

A study of the salts of the aromatic alcohols, such as benzyl alcohol and benzhydrol, from the point of view developed by the work of Nef seemed especially desirable, and, consequently, work in this direction has been undertaken in this laboratory at Dr. Nef's suggestion, and under his guidance, by Mr. Higley and myself. I have confined my experiments chiefly to the benzhydrol series. As Mr. Higley's results in the benzyl series will presumably not be published for some time,[3] I shall at times refer briefly to them where they have a bearing on my own work. A study of the dissociation phenomena in the benzhydrol series seemed of interest first, because Knoevenagel[4] has recently, without sufficient basis, assumed a direct dissociation of benzhydrol into hydrogen and benzophenone, and secondly because it would be possible here to trace quantitatively all the reaction-products with great ease, as they must be crystalline, and their quantitative separation has already been worked out thoroughly by Nef (*loc. cit.*). The experiments performed with sodium benzhydrol were found to be entirely in harmony with the data obtained by Nef. It was possible to alkylate formic, acetic, and isobutyric acids by means of this salt. In the case of the acetic acid a 75 per cent yield

[1] Cf. Nef: Ann. Chem. (Liebig), **318**, 150; Beatty: This JOURNAL, **30**, 224.
[2] Ann. Chem. (Liebig), **318**, 148.
[3] This JOURNAL, **30**, 225, foot-note.
[4] Ber. d. chem. Ges., **36**, 588.

of the monoalkylated acetic acid was actually obtained. These experiments finally led to an investigation of the action of sodium on benzyl acetate and allied compounds, and thus to a complete revision of the work Conrad and Hodgkinson[1] carried out in this direction some twenty-five years ago.

Preparation of Sodium Benzhydrol.—The benzhydrol used in all of my experiments was prepared according to the directions of Nef.[2] It was dissolved in 5 volumes of absolute ether, containing the calculated amount of sodium in the form of wire; the mixture was then heated under a reversed condenser until the metal had all disappeared. On cooling, sodium benzhydrol often crystallized out in large, transparent, colorless, crystalline plates, 2 to 3 cm. in length.

1.3830 grams substance, treated with water, required 65.1 cc. N/10 H_2SO_4 for neutralization.

1.0930 grams substance, treated with water, required 52.1 cc. N/10 H_2SO_4 for neutralization.

	Calculated for $(C_6H_5)_2CHONa$.	Found.	
Na	11.1	10.8	10.9

The salt quickly gains in weight in the air, owing to rapid absorption of water and oxygen; it turns green or greenish-blue in the light, and becomes colorless again over night. This phenomenon was noted for seven successive days, and reminds one of the behavior of benzhydrol ethyl ether described by Linnemann,[3] although I have never noticed these phenomena in the latter case.

Dissociation of Sodium Benzhydrol.—The decomposition-point of this substance lies about 50° below that of benzhydrol, namely, at 250°. The salt, consequently, burns with considerable speed in dry air at the ordinary temperature. The products formed by heating the salt to the dissociating-point are benzene, sodium benzoate, and diphenyl methane, including, at times, also some tetraphenyl ethane and ethylene. Three

[1] Ann. Chem. (Liebig), **193**, 298; **301**, 166.
[2] *Ibid.*, **298**, 231–233.
[3] *Ibid.*, **133**, 6.

experiments were carried out quantitatively under slightly different conditions.

1. Twenty grams of sodium benzhydrol were heated in a distilling-flask for eight and a half hours in a metal bath, at a temperature ranging from 240° to 270°. The distilling-flask was connected with a condenser, a receiver, and an azotometer. The salt became at first bluish in color, but at the end was colorless again. No gaseous products were formed; the receiver contained 3.4 grams of liquid, from which, on fractionation, 2.9 grams of benzene, boiling from 75° to 80°, were obtained. The residue in the distilling-flask was worked up for neutral and acid products by extracting with dilute sodium hydroxide and ether. The ether extract gave, on crystallization from ligroin, 6.2 grams of benzhydrol, melting at 69°, and the filtrate gave 2.5 grams of diphenyl methane. Four and five-tenths grams of benzoic acid were obtained from the alkaline solution.

2. A second experiment, similar to 1, and using the same amount of material, but heating during four hours at 260° to 290°, and for a short time to 300°, showed some blackening and gas evolution (only at 300°). The reaction-products were found to be 3.1 grams of benzene, 4.2 grams of benzoic acid, 7.7 grams of diphenyl methane, 0.5 gram of tetraphenylethylene, 0.4 gram of tetraphenyl ethane, and 1.1 grams of benzhydrol.

Benzophenone was not present in either 1 or 2, as was proved by digestion of the neutral product with alcoholic phenylhydrazine, after removal of the benzhydrol with cold ligroin.

3. Twenty grams of sodium benzhydrol were heated in a sealed tube at 270° to 280° for forty hours (five successive days of eight hours each). No pressure was observed on opening the tube. The residue had a yellowish tinge, and was somewhat blackened in the middle. The reaction-products were determined as 2.6 grams of benzene, 5.5 grams of benzoic acid, 7.3 grams of diphenyl methane, and 3.1 grams of benzhydrol. Therefore, the following main reaction takes place on heating sodium benzhydrol to its decomposition-point:

$$2(C_6H_5)_2CHONa \rightarrowtail 2(C_6H_5)_2C< + 2H-ONa \rightarrowtail$$
$$(C_6H_5)_2C(ONa)_2 + 2H + (C_6H_5)_2C< \rightarrowtail$$
$$(C_6H_5)_2C=O + Na_2O + H_2C(C_6H_5)_2.$$

The reaction is obviously entirely analogous to the one which takes place between benzaldehyde and potassium hydroxide at the ordinary temperature.[1] That under the conditions of the experiment the benzophenone first formed must be rapidly and completely converted into equal amounts of benzene and sodium benzoate,

$$(C_6H_5)_2C=O + NaOH \rightarrowtail C_6H_5COONa + H.C_6H_5,$$

follows from the observations of Chancel[2] on benzophenone, and was also established by special experiment.

An intimate mixture of 10 grams of benzophenone and 2.2 grams of sodium hydroxide were heated for one hour at 260° to 270° (apparatus as in 1, above); 3.6 grams of benzene, boiling from 78° to 80°, were obtained from the distillate in the receiver; the residue in the distilling-flask gave 4.5 grams of benzoic acid.

The small amount of tetraphenylethylene and ethane observed in Experiment 2, above, is probably due to a polymerization of the nascent molecules of diphenyl methylene,

$$(C_6H_5)_2C<,$$

and diphenyl methyl,

$$(C_6H_5)_2CH-.$$

The Spontaneous Combustion of Sodium Benzhydrol in Dry Air.—According to Nef's interpretation of combustion phenomena,[3] the following reaction between the dissociated sodium benzhydrol molecules and the active oxygen molecules of the air must take place at considerable speed on passing dry air and oxygen over sodium benzhydrol at the ordinary temperature:

$$(C_6H_5)_2C< + 2NaOH + \overset{|}{O}\!-\!\overset{|}{O} \rightarrowtail$$
$$(C_6H_5)_2C(ONa)_2 + H_2O_2 \rightarrowtail$$
$$(C_6H_5)_2CO + Na_2O_2 + H_2O.$$

[1] Nef: Ann. Chem. (Liebig), **298**, 301–302.
[2] *Ibid.*, **72**, 280.
[3] *Ibid.*, **298**, 294–301, 322–332; **318**, 177–182.

This was found to be the case. The sodium peroxide is, however, in great part used up in oxidizing the unchanged diphenylmethylene particles,

$$(C_6H_5)_2C< + Na_2O_2 \rightarrowtail (C_6H_5)_2C=O + Na_2O,$$

so that only 21.67 per cent of the sodium peroxide was actually isolated, as such, at the end of the experiment. No trace of a peroxide, $(C_6H_5)_2C<\begin{matrix}O\\|\\O\end{matrix}$, such as would be demanded by Engler and Bach's interpretation of combustion phenomena,

$$NaOH + (C_6H_5)_2C< + \overset{|}{O}\!\!-\!\!\overset{|}{O} \rightarrowtail (C_6H_5)C<\begin{matrix}O\\|\\O\end{matrix} + NaOH,$$

was found in my oxidation experiments. Nef also failed to obtain a trace of the stable acetone peroxide of Baeyer in his experiments on the oxidation of sodium isopropylate.[1]

1. Twenty-five grams of sodium benzhydrol were placed in a large flask and a stream of air, dried by a combustion train, was slowly passed over it. A perceptible rise of temperature was observed after an hour and the gain in weight, after nine hours, was 1 gram. The mass had now a greenish tint and appeared moist. Dry oxygen was then passed over the mixture for ten hours, with no apparent change. The mass was directly extracted with absolute ether; no benzene was present, and the ether extract gave, on fractionation under 25 mm., 16.2 grams of perfectly pure benzophenon eboiling at 180° to 182°. It solidified immediately on addition of a crystal of benzophenone, and then all melted at 47°. A portion, 5 grams, gave, on digestion with 3.7 grams of phenylhydrazine and an equal weight of alcohol, 7 grams of benzophenone phenylhydrazone melting at 137° (theory 7.47 grams). The portion insoluble in ether, 7 grams, was treated with water and extracted with ether. The alkaline solution gave a marked test for carbonic acid, and, on acidifying, 0.8 gram of benzoic acid, melting at 121°, was obtained. The solution also gave a most pronounced test for hydrogen peroxide with

[1] Ann. Chem. (Liebig), 318, 181.

bichromate and ether. On treatment of a portion of the solution with benzoyl chloride, according to v. Pechmann,[1] a precipitate of dibenzoyl peroxide, melting at 104°, was obtained.

2. In order to determine the amount of hydrogen peroxide quantitatively, a fresh oxidation experiment was carried out with 10 grams of sodium benzhydrol. During the oxidation (air eight hours, oxygen forty-four hours) the distilling-flask containing the salt was kept immersed in ice-water. The reaction-products were at once treated with water and an excess of potassium iodide added. The amount of iodine set free was then determined by means of sodium thiosulphate (preliminary experiments having shown that this method was accurate for the work in hand); 0.39 gram of sodium peroxide, or 21.67 per cent of the amount demanded by the above theory, was found.

On the Combustion or Oxidation of Bromdiphenylmethane.— The experiments of Nef have proved that not only primary and secondary alcohols, their salts, and ethers, but also the primary and secondary alkyl haloids, the aldehydes, ketones, fatty acids, substituted ammonias, paraffines, etc., undergo methylene dissociation. Ethane, toluene, diphenyl methane, when first oxidized, give acetaldehyde, benzaldehyde and benzophenone, respectively, because these substances are partially dissociated at the ordinary temperature, *e. g.*,

$$CH_3CH_3 \rightleftarrows CH_2{=}CH_2 + H_2.$$

It was, therefore, of interest to try the action of oxidizing agents on bromdiphenyl methane. This substance possesses, as Nef has shown, a low dissociation-point, 250°. It ought, therefore, to oxidize slowly in dry air, at the ordinary temperature, to benzophenone. Miss Goldthwaite has, indeed, shown that such an oxidation takes place with the analogous paradibromdiphenyl methyl bromide. When, however, either of these compounds is heated to the decomposition-point, 250°, without air access, hydrogen bromide is eliminated quantitatively, but the diphenyl methylene residues first set free either polymerize directly to the dimolecular derivatives, or give

[1] Ber. d. chem. Ges., 27, 1511.

these end-products by an intermediate alkylation and subsequent loss of hydrogen bromide,

$$(C_6H_5)_2C< + HCBr(C_6H_5)_2 \rightarrowtail (C_6H_5)_2CH—CBr(C_6H_5)_2.$$

That the dissociation of these compounds is monomolecular and not bimolecular is furthermore proved by the fact that, when the heating is carried out in a stream of dry air or oxygen, benzophenone and paradibrombenzophenone, respectively, are formed quantitatively. This proves that the diphenyl methylene residues first set free combine preferably with the oxygen to give the corresponding oxides. The reaction is, therefore, perfectly analogous to the combustion of sodium benzhydrol presented above. In the light of what has just been said, the results of the following experiments with bromdiphenyl methane are self-evident:

1. Ten grams of bromdiphenyl methane were treated in the cold, and in a solution acidified with sulphuric acid, with aqueous potassium permanganate until no further decolorization took place. The solution was extracted with ether and the oil obtained was then digested with phenylhydrazine and alcohol. Nine and one-tenths grams of benzophenone phenylhydrazone, melting at 136°, were obtained.

2. Five grams of bromdiphenylmethane were placed in a distilling-flask connected with a reversed condenser and dry oxygen steadily passed through the molten substance, which was heated in a metal-bath at 160° to 170°. Streams of hydrogen bromide came off at first, and practically ceased after three and one half hours' heating. The oil left in the distilling-flask boiled chiefly at 160° to 170° under 10 mm. pressure, and gave, on digestion with phenylhydrazine and alcohol, 5.3 grams of benzophenone phenyl hydrazone melting at 137°. Nine-tenths gram of the tetraphenyl ethylene, melting at 218°, were found in the distilling-flask after the removal of the benzophenone by distillation.

3. Five grams of bromdiphenyl methane, dissolved in absolute ether, were left standing in the cold for two weeks with 3 grams of sodium in the form of wire. One and two-tenths

grams of tetraphenyl ethane and 1.1 grams of diphenyl methane were obtained as reaction-products.

The Action of Sodium Benzhydrol on Benzhydrol Acetate.—As is well known through the work of Geuther, Claisen and others, esters of acetic acid are converted into acetoacetic ether by treatment with sodium or sodium alcoholates. The reaction has been shown by Nef to belong to the category of olefine condensations, and is therefore reversible. In connection with the earlier experiments on the esters of acetic acid, it was found that esters containing an aliphatic group, such as methyl, propyl, and isoamyl acetate, all give a fair yield of the corresponding acetoacetic ester, on treatment with sodium or with sodium alcoholates. On trying the experiment with benzyl acetate and sodium, however, Conrad and Hodgkinson found, to their great surprise, that no trace of acetoacetic benzyl ester was obtained.[1] An interaction between the reagents took place at 135° and then proceeded with some violence. According to their investigations, benzyl hydrocinnamate,

$$C_6H_5CH_2CH_2COOCH_2C_6H_5,$$

is the chief reaction-product. Such a result could now be readily understood in view of the experiments of Nef on the alkylation of the fatty acids by means of sodium alcoholates. The phenyl methylene particles, resulting from the dissociation of the sodium benzylate first formed, must alkylate the unchanged benzyl acetate as follows :[2]

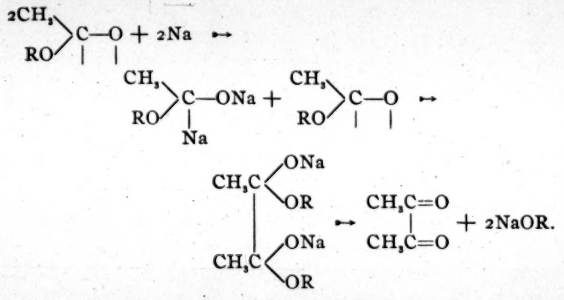
$$C_6H_5CH< + H—CH_2COOCH_2C_6H_5 \rightarrowtail C_6H_5CH_2CH_2COOCH_2C_6H_5.$$

A more careful investigation of the reaction of Conrad and Hodgkinson, which is described in detail below, has proved that much benzyl ether is formed besides benzyl hydrocinnamate. The question now arises, why do not benzyl acetate and sodium interact to give an ester of acetoacetic acid? The same question presents itself in the case of benzhydrol acetate. The problem was first taken up in this laboratory by Shaklee,

[1] Ann. Chem. (Liebig), **193**, 298.

[2] *Ibid.*, **318**, 144; Cf. This JOURNAL, **30**, 225, foot-note.

who proved that benzyl acetate and benzhydrol acetate readily react with sodium in absolute ethereal solution in the cold. He found that very little hydrogen was given off in the course of the reaction, and that the chief products were acetic acid, and benzyl alcohol, or benzhydrol, respectively. In both cases, however, the formation of a small amount of diacetyl was observed. Shaklee established this rigidly by the isolation of the osazone, which was analyzed and found to be identical in its properties with the statements given in the literature. This result, in conjunction with the other facts observed, proves that some esters of acetic acid can react with sodium in a manner entirely different from ethyl acetate. The experiments of Nef on the action of sodium on carbonyl compounds[1] make it exceedingly probable that the following reaction between sodium and acid esters can take place:



No hydrogen is formed in this reaction and the yield of diacetyl must necessarily remain low, because all orthodicarbonyl compounds undergo a benzilic acid rearrangement, *i. e.*, a conversion into glycollic acid derivatives, especially in the presence of strong alkali. It is, therefore, quite probable that dimethylglycollic acid was formed in Shaklee's experiments but was overlooked by him.

The fact that ethyl isobutyrate gives diisopropylglycollic acid derivatives as the chief reaction-products[2] on treatment

[1] Ann. Chem. (Liebig), **308**, 283, 292; Cf. Acree: This JOURNAL, **29**, 588.

[2] Hantzsch: Ber. d. chem. Ges., **20**, 2332; Ann. Chem. (Liebig), **249**, 54; **246**, 129.

with sodium, in absolute ethereal solution, taken in connection with Shaklee's isolation of diacetyl, makes this assumption almost a certainty. These results at once bring up the question whether ethyl acetate itself may, to some extent, not react in an analogous manner with metallic sodium. The amount of hydrogen actually evolved in the manufacture of acetoacetic ether from acetic ether and sodium is only 36.5 per cent of the theoretical amount in the most favorable case.[1] The preliminary experiments which I have carried out in this direction are very striking, and seem to justify these conclusions. When ethyl acetate, carefully dried, is diluted with 10 parts of absolute ether and treated with one atomic proportion of sodium, the metal disappeared entirely after twenty-four hours' standing. Only traces of acetoacetic ether and of hydrogen were obtained under these conditions, although the experiment was tried five times, using 176 grams of ethyl acetate in each experiment. It is the intention of Dr. Nef to investigate this reaction in the near future with the greatest of care. The results obtained show, however, that the recent assumption of Michael[2] that ethyl acetate first gives the salt $CH_3NaCOOC_2H_5$, etc., on treatment with sodium cannot possibly be correct. Experiments in this connection by Higley have further proved that a mixture of 2 molecules of ethyl acetate and 1 molecule of sodium ethylate, on standing for a week at ordinary temperatures, gives a 26.7 per cent yield of acetoacetic ester; on standing for twenty-five days a 36.1 per cent yield of the ester was obtained.[3]

In order to determine why the corresponding condensation between sodium benzylate and benzyl acetate, as well as between sodium benzhydrol and benzhydrol acetate does not take place to any extent, it was obviously first necessary to prepare benzyl- and benzhydrolacetoacetate and study their properties.

Benzyl Acetoacetate, $CH_3COH : CHCOOCH_2C_6H_5$.—This ester has been prepared and analyzed by Shaklee, who obtained it, almost quantitatively, by heating a mixture of 20 grams of

[1] Cf. Meyer: J. prakt. Chem., [2], **68**, 528.
[2] Ber. d. chem. Ges., **33**, 3731.
[3] Cf. E. V. Meyer: J. prakt. Chem., [2], **65**, 528.

benzyl alcohol and 40 grams of acetoacetic ethyl ester in a distilling-flask connected with a condenser and Brühl apparatus. The bath was kept at 160° and as soon as no more ethyl alcohol distilled over, the apparatus was exhausted. Thirty-four grams of benzyl acetoacetate, boiling at 162° to 164° under 16 mm. pressure, was obtained as a colorless mobile oil, smelling like ordinary acetoacetic ester. The oil boils, with some decomposition, at about 270°, gives a blood-red coloration with alcoholic ferric chloride, is insoluble in alkali carbonates, but dissolves without decomposition in cold aqueous sodium hydroxide.

The copper salt, which has been analyzed by Higley, is precipitated quantitatively by means of aqueous alcoholic copper acetate. It crystallizes well from benzene, and melts at 156°. Experiments by Shaklee and Higley have shown that benzyl-acetoacetate is never formed in amounts greater than 2 per cent on treatment of benzyl acetate with sodium or with sodium benzylate under the most varying conditions (20°, 100°, 140°). Higlee's experiments prove, furthermore, that benzyl acetoacetate is readily decomposed by heating it with sodium benzylate at 100° or at a still higher temperature. Consequently only traces of benzyl acetoacetate are obtained from mixtures of benzyl acetate and sodium or sodium benzylate when heated above 100°. These data, therefore, prove that benzyl acetoacetate is formed from its components by the aldol condensation, but in relatively far smaller amounts than ethylacetoacetate. The great difference in the yield, as the reaction is reversible, is simply due to the far greater relative instability of benzyl acetoacetate My own experiments in the benzhydrol series confirm in every way these observations of Higley.

Benzhydrol Acetoacetate, $CH_3COH{:}CHCOOCH(C_6H_5)_2$.—Fifty grams of benzhydrol dissolve in 100 grams of ordinary acetoacetic ether with marked lowering of temperature (23° to 10°). This mixture was heated in an oil-bath at 150° for one hour; much ethyl alcohol distilled over. The oil left in the distilling-flask was now heated *in vacuo* at 200°, the non-volatile portion dissolved in cold sodium hydroxide, and the neutral constituents extracted with ether. The alkaline solution gave,

on acidifying with sulphuric acid and extracting with ether, 51 grams of crude oil, which soon solidified. By crystallizing from ether-ligroin, benzhydrol acetoacetate was obtained in colorless plates, melting at 56°. The substance is very soluble in the ordinary organic solvents except ligroin. It smells like acetoacetic ether and gives a deep purple coloration with ferric chloride. It is insoluble in alkali carbonates and, like all benzhydrol derivatives, gives a deep red coloration with concentrated sulphuric acid.

0.2291 gram substance gave 0.6329 gram CO_2 and 0.1228 gram H_2O.

	Calculated for $CH_3COH:CHCOOCH(C_6H_5)_2$.	Found.
C	76.1	75.4
H	6.0	6.0

The copper salt is precipitated quantitatively by means of aqueous alcoholic copper acetate. It crystallizes from benzene as a powder, melting at 174° to 176°. The following experiments show that, at best, it is possible to obtain benzhydrol acetoacetate only in very small amounts from mixtures of benzhydrol acetate and sodium benzhydrol; this is due, in part or entirely, to the great instability of sodium benzhydrol acetoacetate under these conditions. It may, however, also be due in part to the greater stability of the orthoacetic acid addition-product, $CH_3C(OCH(C_6H_5)_2)_2(ONa)$, which must necessarily be first formed on mixing these reagents.[1]

1. Twenty-two and six-tenths grams of benzhydrol acetate (2 mols.) and 10.3 grams of sodium benzhydrol were intimately mixed. There is a noticeable heat evolution, owing to the formation of the ortho addition-product. The mixture was heated in a sealed tube at 100° for fifteen hours. The mass was then treated with dilute sulphuric acid and worked up as usual for products soluble in sodium hydroxide and sodium carbonate. A small amount of β-diphenylpropionic acid, the monoalkylated acetic acid (see below), was obtained, besides

[1] Claisen: Ber. d. chem. Ges., 20, 648.

acetic acid. The sodium hydroxide solution gave 0.4 gram of benzhydrol acetoacetate, melting at 53°, and identical in its properties with the ester described above. The neutral portion gave 14 grams of benzhydrol, which melted at 68° and crystallized from ligroin. Ten grams of oil, boiling at 176° to 183° under 17 mm. pressure, were also obtained. This was proved to be free from benzophenone by digestion with alcoholic phenylhydrazine. On saponification with alcoholic potash the oil gave 7.8 grams of benzhydrol, hence it consisted of benzhydrol acetate.

2. Five grams of benzhydrol acetoacetate and 8 grams of sodium benzhydrol (2 mols.), treated as in 1, gave 6 grams of benzhydrol and small amounts of benzophenone; the latter was probably formed through a spontaneous oxidation of sodium benzhydrol, as the mixture stood in the air before being worked up. No unchanged benzhydrol acetoacetate was found.

3. Twenty-two and six-tenths grams benzhydrol acetate (4 mols.) and 5.1 grams of sodium benzhydrol, treated as in 1, gave only traces of β-diphenylpropionic acid, 8.5 grams of benzhydrol, and 14.7 grams of unchanged benzhydrol acetate.

4. Ten grams of benzhydrol acetate, dissolved in absolute ether and treated with 7 grams of sodium in the form of wire, reacted completely in the cold. On working up as in 1, 4 grams of benzhydrol and only traces of benzhydrol acetoacetate were obtained. It is to be emphasized that Shaklee obtained also small amounts of diacetyl under similar conditions.

The experiments, 1 to 4, show that mixtures of benzhydrol acetate and sodium benzhydrol or sodium do not interact to give an appreciable amount of benzhydrol acetoacetate. It was now of interest to determine what would happen if molecular amounts of these reagents were heated to a higher temperature (150° to 300°). It is obvious from the experiments of Nef that the dissociated molecules coming first from the sodium benzhydrol, and also from the dissociated benzhydrol acetate (see below), might alkylate the benzhydrol acetate or the sodium acetate,

$$(C_6H_5)_2C< + H—CH_2COOM \rightarrow (C_6H_5)_2CHCH_2COOM,$$

which would result in the formation of β-diphenylpropionate or its benzhydrol ester. The experiment was therefore tried, and, under the most favorable conditions (300°), a yield of 75 per cent of the theoretical amount of β-diphenylpropionic acid was actually obtained.

Benzhydrol β-Diphenylpropionate, $(C_6H_5)_2CHCH_2COOCH(C_6H_5)_2$. — As this ester might be formed by direct alkylation of benzhydrol acetate it was synthesized and studied. On account of the very stable properties ascribed by Conrad and Hodgkinson (*loc. cit.*) to the analogous benzyl hydrocinnamate, it was at first expected that the ester must be exceedingly difficult to saponify. This was found, however, not to be the case, and later experiments (see below) with the real synthetic benzyl hydrocinnamate have proved that it also can be saponified with the greatest of ease by means of alcoholic potassium hydroxide in the cold.

β-Diphenylpropionic acid was prepared according to the directions of Henderson.[1] The melting-point of the acid, after crystallization from ligroin, was found to be 155°, whereas Henderson gives 151°. The acid crystallizes in needles and gives no coloration on standing with concentrated sulphuric acid. It is not volatile with steam. Heated with an equal weight of sodium benzhydrol for six hours, in a sealed tube, at 300° to 310°, it was recovered entirely unchanged. The potassium salt of β-diphenylpropionic acid, dissolved in an equal weight of the free acid, was now heated with the theoretical amount of bromdiphenylmethane for five hours at 150° to 160°. The neutral product thus obtained, which was insoluble in cold ether and soluble in cold benzene, was recrystallized from alcohol and colorless needles, melting at 112°, were obtained. The ester is difficultly soluble in ether and cold alcohol, but very soluble in benzene.

0.1831 gram substance gave 0.5747 gram CO_2 and 0.1072 gram H_2O.

[1] J. Chem. Soc. (London), **59**, 734.

	Calculated for $(C_6H_5)_2CHCH_2COOCH(C_6H_5)_2$.	Found.
C	85.7	85.4
H	6.1	6.2

Benzhydrol β-diphenylpropionate was saponified with the greatest ease by heating 5 grams in an oil-bath at 110°, for one hour, with 1.25 mol. potassium hydroxide in 10 grams alcohol. Two grams of benzhydrol and 2.5 grams of β-diphenylpropionic acid (theory 2.8 grams), melting at 154°, were obtained as reaction-products.

On the Alkylation of Acetic Acid by Sodium Benzhydrol.—This was accomplished in a variety of ways, all of which depend on the same principle, namely, the absorption of an acetate by diphenylmethylene coming from the dissociation of a benzhydrol salt. The following experiments need, therefore, no further elucidation:

1. Ten grams of ethyl acetanilide and 12 grams of sodium benzhydrol were carefully mixed in a sealed tube until homogeneous, and were then heated for eight hours at 160° to 170°, and finally for three hours at 220°. The reaction-products were found to be as follows: 6.5 grams of ethyl aniline, 6.1 grams of benzhydrol, 1.1 grams of benzhydrol ether, traces of tetraphenyl ethane, and a small amount of benzophenone (identified as phenylhydrazone, 1.7 grams melting at 136°, being obtained). The solid acid product was found to consist only of β-diphenylpropionic acid (1.1 grams melting at 155°).

2. A second experiment, using 10 grams of ethyl acetanilide and 15 grams sodium benzhydrol, gave, after heating in a sealed tube for fifty hours (in periods of about eight hours daily), 6.5 grams of ethyl aniline, 5.2 grams benzhydrol, 1.5 grams of β-diphenylpropionic acid, 1.4 grams of tetraphenylethane, and a small amount of benzophenone (1.2 grams of phenylhydrazone being isolated).

3. 25 grams of benzhydrol acetate and 7 grams of quicklime were intimately mixed and heated in a sealed tube for six hours at 230° to 250°. Four-tenths gram of β-diphenylpropionic acid, 7.5 grams of tetraphenylethane, 6 grams of benzhydrol ether, 3.2 grams of benzhydrol, besides a small amount

of benzophenone (4.1 grams phenylhydrazone) were obtained as reaction-products.

This experiment is of interest in connection with the formation of *n*-butyric acid, observed by Ljubawin,[1] on heating ethyl acetate with quicklime at 250° to 280°. Calcium ethylate and acetate are obviously first formed,

$$2CH_3COOCH_2CH_3 + 2CaO \rightarrow Ca(OCOCH_3)_2 + Ca(OCH_2CH_3)_2$$

the ethylidene, resulting from the dissociation of calcium ethylate, alkylates the acetate, giving calcium butyrate.

4. An intimate mixture of 16 grams benzhydrol acetate and 20 grams of sodium benzhydrol was heated for thirty hours, in a sealed tube, at 150° to 160°. There was no pressure on opening the tube, and 1.5 grams β-diphenylpropionic acid, besides 3.1 grams of benzhydrol β-diphenylpropionate were obtained. The other products were 19 grams benzhydrol, 1.5 grams benzhydrol ether, 1 gram tetraphenylethylene, traces of tetraphenylethane and a small amount of benzophenone.

5. Twelve grams of benzhydrol acetate and one atomic proportion of sodium (1.2 grams) were heated under a reversed condenser. There was no action at 100°; as soon as the bath reached 130° to 140° the metal dissolved rapidly and, after an hour's heating at that temperature, the following products were obtained: 1.1 grams β-diphenylpropionic acid, 6.5 grams of benzhydrol, 0.5 gram tetraphenylethylene, besides traces of the corresponding ethane derivative, and benzophenone (3.1 grams phenylhydrazone).

It will be noticed that the yield of monoalkylated acetic acid obtained in experiments 1 to 5 is not very large. At first this was attributed to a decomposition of this acid because Nef has shown that the fatty acids have comparatively low dissociation points.[2] Furthermore, the fact observed by Karsten[3] that β-diphenylpropionic acid gives benzophenone by oxidation with potassium permanganate points to a possible dissociation

[1] Jour. Russ. Chem. Ges., **12**, 81.
[2] Ann. Chem. (Liebig), **318**, 220.
[3] Ber. d. chem. Ges., **26**, 1579.

of the acid into diphenylmethylene and acetic acid. On further study, however, β-diphenylpropionic acid was found to be an exceedingly stable substance, with a decomposition-point certainly above 400°. The following experiment with benzhydrol acetate and sodium benzhydrol proves finally that the yield of monoalkylated acetic acid can be increased to 75 per cent of the theoretical amount by simply heating higher, namely, to 300°.

Ten grams benzhydrol acetate and 20 grams of sodium benzhydrol were mixed as thoroughly as possible in a sealed tube and then heated to 300° to 310° for six hours. The temperature accidentally ran up to 350° for a very short time. The result was 7.5 grams β-diphenylpropionic acid, 0.2 gram benzoic acid, 4 grams diphenylmethane, and benzophenone (6.5 grams phenylhydrazone).

It should be emphasized at this point that, aside from the formation of β-diphenylpropionic acid by direct alkylation, with or without the intermediate formation of an acetoacetic acid derivative, another possible interpretation presents itself and was carefully considered. The benzophenone first formed by the decomposition of the sodium benzhydrol (see above),

$$(C_6H_5)_2C< + 2HONa \rightarrow (C_6H_5)_2C{=}O + Na_2O + 2H,$$

might act as such with the benzhydrol acetate by addition, thus:

$$(C_6H_5)_2C(-O-)_2 + HCH_2COOCH(C_6H_5)_2 \rightarrow$$

$$(C_6H_5)_2C\begin{cases} CH_2{-}COOCH(C_6H_5)_2 \\ OH \end{cases},$$

the resulting β-oxydiphenylpropionate must then lose water and take up 2 atoms of hydrogen to give β-diphenylpropionic acid. This interpretation is *à priori* highly improbable, for a variety of reasons, which need hardly be discussed in detail here. Suffice it to state that I made many attempts to condense benzophenone with salts of acetic and isobutyric acids, but without positive results. Furthermore, the following experiments were carried out in order to ascertain whether the

yield of alkylated fatty acid is increased by an addition of benzophenone :

1. An intimate mixture of 10 grams of benzhydrol acetate, 10 grams of sodium benzhydrol and 5 grams benzophenone was heated in a sealed tube for six hours at 300°. Three and nine-tenths grams of β-diphenylpropionic acid, 3.5 grams diphenylmethane, 3.8 grams of benzhydrol and benzophenone (9 grams of phenylhydrazone) were obtained.

2. An intimate mixture of 10 grams benzhydrol acetate and 10 grams of sodium benzhydrol was heated in a sealed tube at the same time and in the same furnace as used in 1. The products formed were 3.4 grams β-diphenylpropionic acid, 3.4 grams benzhydrol, 4 grams diphenylmethane, and benzophenone (4.5 grams phenylhydrazone).

These experiments show very clearly that a considerable portion of the sodium benzhydrol decomposes as such (see above),

$$2(C_6H_5)_2CHONa \rightarrow (C_6H_5)_2C{=}O + Na_2O + (C_6H_5)_2CH_2,$$

giving benzophenone and diphenylmethane, and these are found mostly unchanged at the end of the experiment. This explains why it is necessary to use more than 1 molecular proportion of sodium benzhydrol in order to obtain a very large yield of β-diphenylpropionic acid (see above experiment with 2 molecular proportions of alcoholate at 300° to 310°). The slightly larger yield of monoalkylated acetic acid obtained in experiment 1, as compared with experiment 2, is easily understood because a portion of the benzophenone added must necessarily be reduced to benzhydrol[1] by the atomic hydrogen set free by the action of diphenylmethylene on sodium hydroxide. For that reason also the amount of diphenylmethane obtained in 1 is proportionally less than that found in 2.

The reactions under consideration therefore unquestionably belong to the category of alkylation phenomena. That the acetyl radical is alkylated directly by the diphenylmethylene particles, and not indirectly through an intermediate acetoacetic ether formation, is in the highest degree probable from

[1] Cf. Nef : Ann. Chem. (Liebig), **318**, 183.

the data presented above on the benzyl and benzhydrol acetoacetate.

There are, however, undoubtedly some cases where the alkylation depends partially or entirely on an intermediate formation of acetoacetic acid derivatives, and other cases where it is impossible to decide decisively between these two possibilities—which necessarily, however, lead to the same end result.

Furthermore, there is no doubt that the hydrogen atom in formic acid derivatives, X—C(=O)H, and the tertiary hydrogen atom in isobutyric acid derivatives, X—CO—C(=$(CH_3)_2$)H, is capable of direct alkylation by diphenylmethylene, as is shown by the following experiments:

Alkylation of Benzhydrol Formate.—Benzhydrol formate is readily obtained by heating a solution of 20 grams of potassium formate and 50 grams of bromdiphenylmethane, in formic acid, in a sealed tube, at 100°, for about ten hours. The benzhydrol formate was obtained as a neutral, colorless oil, boiling at 159° to 160° under 10 mm. pressure. An intimate mixture of 10 grams of this oil with 12 grams of sodium benzhydrol was heated in a sealed tube for eight hours, at 300° to 310°, and on working up for acids 0.2 gram pure diphenyl acetic acid, melting at 146°, were obtained; it was recrystallized from water and ligroin and coincided in its properties with those given in the literature.[1] It is quite probable that a much larger yield could be obtained by further work.

Benzhydrol Isobutyrate, $(CH_3)_2CHCOOCH(C_6H_5)_2$.—A mixture of 50 grams bromdiphenylmethane, 30 grams potassium isobutyrate, and 50 grams isobutyric acid was heated under a reversed condenser for one hour at 150°; on pouring into water, extracting with ether, washing with sodium hydroxide, and drying the ethereal solution with calcium chloride, 58 grams of benzhydrolisobutyrate, boiling at 185° to 187° under

[1] Klingemann: Ann. Chem. (Liebig), **275**, 84; Zincke: *Ibid.*, **171**, 122; Dunlap: This JOURNAL, **19**, 645.

15 mm. pressure, were obtained. The oil soon changed to a colorless solid which melted at 54°, is quite soluble in cold alcohol and ether, and can be crystallized from low-boiling ligroin.

0.1912 gram substance gave 0.5623 gram CO_2 and 0.1239 gram H_2O.

	Calculated for $(CH_3)_2CHCOOCH(C_6H_5)_2$.	Found.
C	80.3	80.2
H	7.1	7.2

Alkylation of Benzhydrolisobutyrate, 1-Dimethyl-2-diphenylpropionic Acid, $(C_6H_5)_2CHC(CH_3)_2COOH$.—Nef's experiments with sodium isobutyrate and benzophenone at 190° to 220° have already proved that isobutyric acid is capable of alkylation by diphenylmethylene, and the following experiments simply confirm his results :[1]

1. An intimate mixture of 15 grams of benzyl isobutyrate and 25 grams of sodium benzhydrol was heated in a sealed tube, for five hours, at 190° to 220°. The following products were obtained : 0.8 gram of 1-dimethyl-2-diphenylpropionic acid, in plates, from ligroin, melting at 134° ; 22 grams of benzhydrol ; 4 grams of diphenylmethane ; and benzophenone (4 grams of phenylhydrazone).

2. Twenty-two grams benzhydrol isobutyrate and 15 grams of sodium benzhydrol were heated in a sealed tube, for twenty-six hours, at 100°. Three grams of isobutyric acid and 0.3 gram of monoalkylated isobutyric acid were obtained, besides 16 grams of benzhydrol, 3 grams of diphenylmethane, and 10 grams of unchanged benzhydrol isobutyrate.

3. Fifteen grams each of benzhydrol isobutyrate and sodium benzhydrol were heated in a sealed tube for two and one-half hours, at 270° to 275°. There was some pressure on opening the tube. One-tenth gram benzoic acid and 2.7 grams of 1-dimethyl-2-diphenylpropionic acid (separated by distillation with steam) were obtained. The neutral products were 6 grams of benzhydrol, 4.7 grams of diphenylmethane, and benzophenone (2.4 grams phenylhydrazone).

[1] Ann. Chem. (Liebig), 318, 184.

4. Ten grams of benzhydrol isobutyrate and 20 grams of sodium benzhydrol were heated in a sealed tube, for twenty hours, at 200° to 220°. Only 0.8 gram of monoalkylated isobutyric acid was obtained. The other products were 22 grams benzhydrol, 3 grams diphenylmethane, and benzophenone (5.9 grams phenylhydrazone).

5. Ten grams of benzhydrol isobutyrate and 15 grams sodium benzhydrol were heated in a sealed tube, for eight hours, at 300° to 310°. Four grams of benzoic acid and 3.1 grams monoalkylated isobutyric acid were obtained. The neutral portion gave 6.1 grams of diphenylmethane, and benzophenone (5.9 grams phenylhydrazone).

6. Ten grams benzhydrol isobutyrate and 20 grams sodium benzhydrol heated in a sealed tube, for eight hours, at 270° to 300°, gave 6.3 grams of benzoic acid and 2.8 grams of 1-dimethyl-2-diphenylpropionic acid, 8.2 grams diphenylmethane, 1.2 grams benzhydrol and benzophenone (3.6 grams phenylhydrazone) were obtained from the neutral portion.

The experiments 1 to 6 show that, at best, the yield of monoalkylated isobutyric acid is about 30 per cent; the sodium benzhydrol, in great part, decomposes, as such, by heating, and therefore about equal molecules of diphenylmethane and benzophenone (or its decomposition-products) are always obtained.

The Dissociation of Benzhydrol Acetate.—Nef's experiments have proved that benzhydrol and its derivatives, such as benzhydrol ether, benzhydrol ethyl ether, benzhydrol acetate, benzoate, etc., all dissociate at 300° into diphenylmethylene.[1] This explains why, with concentrated sulphuric acid, all these compounds, as well as benzilic acid, give the same deep red coloration which is simply due to the formation of polymerized diphenylmethylene particles. Preliminary experiments by Nef with benzhydrol acetate[2] have shown that this substance decomposes at 300°, giving acetic acid, tetraphenylethylene, and ethane. I have studied this reaction more in detail, with larger amounts of material. Twenty-five grams of benzhydrol acetate were heated in a sealed tube, at 300° to 310°, for

[1] Ann. Chem. (Liebig), 298, 231–245.
[2] *Loc. cit.*, p. 244.

twenty-four hours, *i. e.*, for three days of eight hours each No pressure was noticed on opening the tube, but the contents were dark-colored and gave a strong odor of acetic acid.

On adding sodium hydroxide and ether a portion remained insoluble and was filtered off and dissolved in cold benzene. Tetraphenylethane must, therefore, be absent. The benzene extract gave, on addition of alcohol, 10.8 grams of pure tetraphenylethylene, melting at 221°. Not a trace of β-diphenylpropionic acid (monoalkylated acetic acid) could be found in the alkaline solution. The ether extract gave, on fractionation under 10 mm. pressure, 4.9 grams of oil boiling at 140° to 170°. This, on treatment with alcoholic phenylhydrazine, yields 2.5 grams of benzophenone phenylhydrazone, melting at 137°, and 2.1 grams of diphenylmethane boiling at 255° to 260°.

The experiment just described shows that 60 per cent of the benzhydrol acetate decomposes as follows:

$$2(C_6H_5)_2CHOCOCH_3 \rightarrowtail (C_6H_5)_2C:C(C_6H_5)_2 + 2CH_3COOH.$$

The formation of tetraphenylethylene may be due to a direct polymerization of the diphenylmethylene particles as such, or is more probably due to an alkylation of the non-dissociated benzhydrol acetate by the diphenylmethylene,[1]

$$(C_6H_5)_2C< + H—C\begin{matrix}(C_6H_5)_2\\ OCOCH_3\end{matrix} \rightarrowtail (C_6H_5)_2CHC\begin{matrix}(C_6H_5)_2\\ OCOCH_3\end{matrix},$$

with subsequent loss of acetic acid from the addition-product thus formed.

A portion of the diphenylmethylene particles probably also act with the acetic acid as follows:

$$(C_6H_5)_2C< + 2H—OCOCH_3 \rightarrowtail (C_6H_5)_2C(OCOCH_3)_2 + 2H + (C_6H_5)_2C{=}O + (CH_3CO)_2O + 2H.$$

The atomic hydrogen thus set free is at once absorbed by more diphenylmethylene to give diphenylmethane. This explains, in an adequate manner, the formation of benzophenone and

[1] Cf. Nef: Ann. Chem. (Liebig), 335, 261.

diphenylmethane in the dissociation experiment with benzhydrol acetate described above.

Nef has repeatedly called attention to the fact that catalytic agents increase, to a very marked extent, the percentage of dissociated particles present at a definite temperature. The following experiment is of interest in this connection: On May 1st, 1903, I placed in the sunlight a sealed tube containing 10 grams of molten benzhydrol acetate. The liquid soon assumed a yellow color with greenish tinge. The tube stood until Oct. 19th, of the same year, and by that time a considerable amount of solid had separated. A strong odor of acetic acid was noticed on opening the tube; 1.7 grams of tetraphenylethylene, melting at 222°, besides acetic acid and 7.5 grams of unchanged benzhydrol acetate were the only reaction-products obtained.

A preliminary experiment with benzhydrol ethyl ether has shown that it decomposes on heating at 300°, in a distilling-flask, without air access, into acetaldehyde, tetraphenylethane, and benzophenone.[1]

Finally, in this connection, I should like to make some remarks on the dissociation of dibenzyl sulphide, which has recently been worked out by Fromm and Achert.[2] These chemists obtained hydrogen sulphide, toluene, stilbene, thionessal (tetraphenylthiophene), and *s*-tetraphenylbutane as decomposition-products. The results are easily understood on the basis of a primary dissociation of benzyl sulphide into hydrogen sulphide and 2 molecules of phenylmethylene. Dibenzyl has also been noticed as a decomposition-product by previous observers, but not by Fromm and Achert. This was probably due to the fact that, in their experiments, the dibenzyl first formed was entirely alkylated by phenylmethylene as follows:

[1] Cf. Goldthwaite: This JOURNAL, 30, 447.
[2] Ber. d. chem. Ges., 36, 534.

The following experiment, in which *s*-tetraphenylbutane is obtained from benzyl chloride by simply heating it with dry potassium oxalate, is evidence in favor of the view just presented.

An intimate mixture of 20 grams benzyl chloride and 35 grams anhydrous potassium oxalate was heated in an oil-bath, at 160°, for four hours. By treating the mass with water a small amount of solid remained undissolved. On crystallizing this from a mixture of acetone and alcohol, 1.8 grams of *s*-tetraphenylbutane, melting at 254° to 255°, were obtained in the form of pearly scales.

On the Action of Sodium on the Benzyl Esters of Acetic, Propionic, Butyric, and Isobutyric Acids—A Revision of Conrad and Hodgkinson's Work.—The experiments of Conrad and Hodgkinson on the action of sodium on the benzyl esters of the acids just named[1] whereby, apparently, the α-monobenzylated derivatives of these esters are obtained as the chief reaction-products have already been briefly discussed above. Such an alkylation is entirely in harmony with the data accumulated by Nef and with my own observations on the action of sodium or sodium benzhydrol on benzhydrol acetate and isobutyrate, respectively. The properties ascribed by Conrad and Hodgkinsin to the esters obtained are, however, so unusual that it seemed very doubtful whether the substances actually prepared had the constitutions assigned to them. The esters in question are all mentioned as being capable of only very slight saponification, even after prolonged digestion with alcoholic potassium hydroxide, or by treatment with soda-lime at higher temperatures. The simplest way to test this point was obviously to synthesize benzyl hydrocinnamate, and then to compare it with the main reaction-product obtained by Conrad and Hodgkinson from sodium and benzyl acetate. This was accordingly done, and the synthetic product was found to behave in an entirely different manner toward alcoholic potassium hydroxide.

Synthesis and Properties of Benzyl Hydrocinnamate, $C_6H_5CH_2CH_2COOCH_2C_6H_5$. — Hydrocinnamic acid was con-

[1] Ann. Chem. (Liebig), **193**, 298; **201**, 166.

verted into the silver salt by neutralization with ammonia and precipitation with aqueous silver nitrate. The salt was purified by crystallization from hot water, well dried and then heated in a sealed tube, for eight hours, at 100°, with the calculated amount of benzyl chloride, diluted with 2 volumes of absolute ether. Benzyl hydrocinnamate was obtained as a colorless oil, boiling at 190° to 195° under 10 mm. pressure.

0.1527 gram substance gave 0.4463 gram CO_2 and 0.0920 gram H_2O.

	Calculated for $C_6H_5CH_2CH_2COOCH_2C_6H_5$.	Found.
C	80.0	79.7
H	6.7	6.7

Ten grams of this oil were at once mixed with the theoretical amount of alcoholic potash and allowed to stand for two hours in the cold. Reaction took place at once, on working up the mixture 3.7 grams of benzyl alcohol, boiling at 204° to 208°, and 5 grams of hydrocinnamic acid, crystallized from ligroin and melting at 48°, were obtained. This striking ease of saponification of benzyl hydrocinnamate is not surprising in view of the statement of Erlenmeyer,[1] "the ethyl ester of hydrocinnamic acid is formed with marvelous ease, likewise it turns acid simply by contact with moist air."

Repetition of Conrad and Hodgkinson's Experiment with Sodium and Benzyl Acetate.—As mentioned above, benzyl acetate and sodium react, in absolute ethereal solution, at ordinary temperatures, giving chiefly sodium benzylate and acetate besides small amounts of diacetyl and benzyl acetoacetate (not over 2 per cent).

A mixture of 100 grams benzyl acetate and 7 grams of sodium, cut in pieces about the size of a pea, does not interact in the cold. It was, therefore, heated, under a reversed condenser, in an oil-bath, with a thermometer in the mixture. As soon as the inside temperature reached 125° a reaction was noticed; the oil-bath was at once removed, the reaction proceeded with violence and the temperature rose to 185°. It is essential for success that there be a great rise of temperature,

[1] Ann. Chem. (Liebig), 137, 330.

as previous experiments have proved that, when smaller amounts of material are used and when care is taken to have the reaction proceed more slowly, practically no high boiling products at all are obtained. Even in the experiment just described my yield of high-boiling material was smaller, comparatively, than that given by Conrad and Hodgkinson. The reaction was completed in twenty minutes, and the dark-brown mixture in the flask was treated with dilute sulphuric acid and extracted with ether. The ether extract was then successively extracted with sodium carbonate and sodium hydroxide and thus resolved into acid and neutral products. One and one-tenth grams of cinnamic acid, melting at 131°, were found in the carbonate solution. The caustic alkali gave a small amount of oil having the properties of benzyl acetoacetate. The main reaction-products were found to be neutral in character, and were fractionated twice under 10 mm. pressure. A small amount of toluene, boiling at 105° to 108° under ordinary pressure, was obtained from the first fraction; then came 71 grams of oil boiling from 90° to 100° under 10 mm. pressure. This was obviously what Conrad and Hodgkinson considered to be unchanged benzyl acetate. It consists, however, chiefly of benzyl alcohol. The first fractions, 30 grams, had only the faintest odor of benzyl acetate. The 71 grams of oil obtained gave, furthermore, on treatment with 1.25 mol. alcoholic potassium hydroxide in the cold, 62 grams of pure benzyl alcohol, boiling at 204° to 206°. On further fractionation of the residue in the distilling-flask, 12 grams of oil, boiling at 160° to 190° under 10 mm. pressure, were obtained, and some tar. This oil was now digested for two hours with 3 grams alcoholic potash at 110°, and on working up for neutral and acid products, 3.4 grams of crude hydrocinnamic acid, boiling at 275° to 290°, were obtained. It soon solidified, and gave, on crystallization from ligroin (b. p. 70° to 80°), 3 grams of the pure acid melting at 47°. The neutral portion, distilled twice under 13 mm. pressure, gave 3.2 grams of benzyl alcohol, boiling at 95° to 100°, and 4 grams oil boiling at 155° to 165°. The latter was proved to be benzyl ether by comparison with a synthetic

product[1] (b. p. 167° to 168° under 15 mm. pressure), and also by analysis:

0.1922 gram substance gave 0.5962 gram CO_2 and 0.1245 gram H_2O.

	Calculated for $(C_6H_5CH_2)_2O$.	Found.
C	84.8	84.6
H	7.1	7.2

From the above data it is obvious that two-thirds of the high-boiling oil consisted of benzyl hydrocinnamate and the remaining third of benzyl ether. Judging from their data, Conrad and Hodgkinson must have had relatively far more benzyl ether in their high-boiling oil. It should be emphasized here that benzyl ether burns with great difficulty; furthermore, that, according to repeated observations of Nef, mixtures of benzyl alcohol and benzyl ether, containing also some phenyl methylene, are very hard to separate completely by fractional distillation under ordinary pressure. Finally, it is clear from the facts presented in this paper that the neutral and high-boiling products obtained by Conrad and Hodgkinson, after treatment with alcoholic potassium hydroxide, must, in all cases, have consisted largely of benzyl ether.

Benzyl Isobutyrate and Sodium Benzylate.—As the action of sodium on benzyl derivatives, in Conrad and Hodgkinson's experiments, obviously depends on the intermediate formation of sodium benzylate, and, owing to the resulting high temperature, on the subsequent alkylation by the phenylmethylene of the products present, the following experiment was carried out in the expectation that a benzylated isobutyric acid would result:

An intimate mixture of 20 grams benzyl isobutyrate and 15 grams sodium benzylate was heated in a sealed tube, for four hours, at 300° to 310°, and then worked up for acid and neutral products: 4 grams of isobutyric acid, 5.8 grams of benzoic acid melting at 122°, but no trace of an α-benzylated isobutyric acid was obtained. The neutral portion contained traces of benzaldehyde, as proved by the isolation of 0.2 gram

[1] Lowe: Ann. Chem. (Liebig), 241, 374.

of phenylhydrazone melting at 156°. The main products were, however, 6.1 grams of benzyl alcohol boiling at 94° to 100° under 10 mm. pressure, and benzyl ether, 8.1 grams, boiling at 130° to 170° under the same pressure. The latter was practically unaffected by digestion with alcoholic potash at 150°. On refractionation, under 8 mm. pressure, 2 grams of oil boiling at 150° to 159°, and 3.5 grams of oil boiling at 159° to 160°, were recovered. Analysis of the latter showed that it was pure benzyl ether.

0.1793 gram substance gave 0.5562 gram CO_2 and 0.1146 gram H_2O.

	Calculated for $(C_6H_5CH_2)_2O$.	Found.
C	84.8	84.6
H	7.1	7.1

According to Lowe (*loc. cit.*), benzyl ether gives toluene and benzaldehyde on prolonged heating at 315°. I have found that pure benzyl ether very slowly yields toluene and benzoic acid on prolonged digestion with alcoholic potassium hydroxide at 150°, or on heating with solid potassium hydroxide or soda-limeat 200°.

It is noteworthy that, in the reaction just described, a large amount of benzyl ether, but not a trace of α-benzylated isobutyric acid is obtained. The corresponding reaction with sodium benzhydrol and benzhydrol isobutyrate, at 300°, gave a 30 per cent yield of monoalkylated isobutyric acid (see above).

Finally, it is to be emphasized here that the substance described by Hodgkinson[1] as α-benzylated isobutyric benzyl ester is exceedingly stable toward alcoholic potash and never gave α-benzylated isobutyric acid by saponification under any conditions. I therefore consider it extremely probable, in view of the data just presented, that Hodgkinson's substance in reality consisted simply of benzyl ether. He succeeded, for instance, in obtaining from it, by means of soda-lime at 200°, toluene and benzoic acid.

In conclusion, I desire to thank Dr. Nef for his painstaking scrutiny and his inspiring interest in connection with this work.

[1] Ann. Chem. (Liebig), 201, 166.

DIE GALVANOPLASTIK. Von DR. W. PFANHAUSER, Fabrikant von Maschinen, Apparaten, und Chemischen Präparaten für Elektroplattierung, Galvanoplastik, und Metallpolierung. Mit 35 in dem Text gedruckten abbildungen. Halle, a. S.: Verlag von Wilhelm Knapp. 1904. pp. 138.

This little monograph on applied electrochemistry deals with its subject under the following general heads. The various "forms" that are used, such as the metals, wax, guttapercha, gypsum, etc., are considered.

The means of conducting the current are then discussed, such as covering the material in question with graphite or with a thin layer of metal.

The different baths that are employed, the choice of anodes, and the arrangement of apparatus are then taken up and treated at sufficient length to be clearly intelligible to any one who has even an elementary knowledge of technical electrochemistry. The monograph can be recommended to all who are interested in this subject. H. C. J.

ELECTROLYTIC COPPER REFINING. By TITUS ULKE, M.E., Consulting Electrochemist. Member of the Amer. Electrochem. Soc. and Amer. Inst. Min. Engineers. New York: John Wiley & Sons. 1904.

DIE ELEKTROLYTISCHE RAFFINATION DES KUPFERS. Von TITUS ULKE. Ins Deutsche übertragen von VIKTOR ENGELHARDT, Ober-Ingenieur und Chemiker der Siemens & Halske, A. G., Wien. Halle, a. S.: Druck und verlag von Wilhelm Knapp. 1904. pp. 152. Price, 8 marks.

This small book is made up largely of articles which have been published in *Mineral Industry*. It contains a good deal of valuable information and is instructive to those who know enough about the refining of copper to enable them to weed out the true from the misleading statements. I. R.

A LABORATORY MANUAL OF ORGANIC CHEMISTRY FOR BEGINNERS. By DR. A. F. HOLLEMAN, Professor Ordinarius in the University of Groningen, Netherlands, and Fellow of the Royal Academy of Sciences, Amsterdam. An Appendix to the Author's Text-book of Organic Chemistry. Translated from the Dutch by A. JAMIESON WALKER, PH.D. (Heidelberg), B.A., Head of the Department of Chemistry, Technical College, Derby, England, with the co-operation of the Author. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904. 12mo. pp. xiv + 78 Cloth. Price, $1.00 net.

The author of this little book seems to think that the idea of working with the compounds of carbon in the laboratory as a part of a course in organic chemistry is rather a new one. It may be in the Netherlands. It is not elsewhere. The author's text-book of organic chemistry is an excellent book

and has been highly spoken of in this JOURNAL,[1] but the laboratory manual is much less satisfactory. A laboratory manual ought to be a safe guide for the student in the laboratory. If it leaves everything to the teacher, it fails of its purpose. The directions here given are so meager that a student would certainly fail in his efforts to perform the experiments unless his teacher should give him a lot of supplementary directions. Take acetaldehyde, for example, page 20. These are the directions: "A mixture of 60 grams of water, 20 grams of concentrated sulphuric acid, and 15 grams of 90 per cent alcohol is added to 13 grams of potassium dichromate contained in a 200 cc. fractionating flask connected with a condenser. Sometimes the oxidation begins spontaneously. Should it not, however, the flask is gently heated on a sand-bath, with a rapid current of cold water flowing through the condenser. A mixture of water, alcohol, acetaldehyde, and acetal distils, and can be used in carrying out the aldehyde-reactions described in 2, 3, and 4." If the experience of thirty odd years is worth anything, that experiment is doomed to failure.

Under formic acid nothing is said about the temperature to which the mixture of glycerol and oxalic acid is to be heated. Similar criticisms are applicable to practically all the directions given in the book. It is hard to see what purpose it will serve that is not much better served by several other books already in use. I. R.

DIE ELEKTROCHEMISCHE REDUKTION DER NITRODERIVATE ORGANISCHER VERBINDUNGEN IN EXPERIMENTELLER UND THEORETISCHER BEZIEHUNG. By JOH. MÖLLER. Halle, a. S.: Wilhelm Knapp. 1904.

This small book of 113 pages, exclusive of the excellent index, gives an interesting account of the results that have been attained in its field. The application of the electric current in organic synthesis has been developed chiefly during the last seven years, and at present a large number of important substances are prepared in this way. Mixed azo compounds and many others can be obtained with greater ease, or in some cases, only by this method. The points of chief importance are the proper selection of current strength, the character and material of the electrodes, and, at times, the use of different condensing agents to stop the action at the desired phase. According to the conditions, the products may be either primary or secondary. In the first case the ions, after losing their charges, combine with one another, as in

[1] This JOURNAL, 31, 190.

Kolbe's classical synthesis of ethane by the electrolysis of potassium acetate solution. When of a secondary nature, the products are formed by the oxidatian or reduction of the discharged ions, or by the action of other substances that may be present in the solution. For instance, when alcoholic solution of potassium chloride is electrolyzed, chloral is obtained probably according to the equations:

$$\text{I.}\quad CH_3.CH_2.OH + 2Cl = 2HCl + CH_3.COH,$$

or $$CH_3.CH_2.OH + O = H_2O + CH_3.COH;$$

and $$\text{II.}\quad CH_3.COH + 6Cl = 3HCl + CCl_3.COH.$$

In like manner, when nitrobenzene, in solution of alcoholic hydrochloric acid, is hydrolyzed, phenyl hydroxylamine is obtained which is then acted on by hydrochloric acid, giving phenyl chloramine. The method evidently is one with great possibilities for nitroso, hydroxylamine, azoxy, azo, hydrazo, amino, aminoxy, diaminodiphenyl, and benzidine derivatives are obtained when nitro compounds are electrolyzed. With the exception of the last class, all of these can be formed in alkaline, as well as in acid solution.

In the first part of the book the methods employed in carrying out reductions in acid and alkaline solution are given in detail. Then follows a discussion of the theories proposed by Haber,[1] Chilesotti,[2] and Löb,[3] to account for the observed phenomena.

The book is one that should be in the hands of every one who wishes to become informed on the subject. It is clearly written, and there are numerous references to the literature. It is hardly necessary to say that it is well printed.

C. E. W.

[1] Ztschr. Elektrochem., 1897-98, p. 506.

[2] *Ibid.*, 1900-01, p. 768.

[3] "Unsere Kenntnisse in der Elektrolyse und Elektrosynthese organischer Verbindungen," p. 63.

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